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(54) BALLISTIC RESISTANT AND FIRE RESISTANT COMPOSITE ARTICLES

BALLISTISCH WIDERSTANDSFÄHIGE UND FEUERBESTÄNDIGE VERBUNDARTIKEL

ARTICLES COMPOSITES RESISTANT AU FEU ET AUX BALLES

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(56) References cited:
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GB-A- 2 347 112
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US-A- 4 822 657

EP 1 560 709 B1

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] This invention relates to ballistically resistant and fire resistant composite articles, more particularly, for use in aircraft interiors, as well as other applications.

2. Description of the Related Art

[0002] Materials used in aircraft compartment interiors are regulated by Title 14 of the Code of Federal Regulations, Part 25. Until recently, the principal concern relating to such materials was fire resistance. However, in the wake of the aircraft hijackings of September 11, 2001, by suicidal terrorists, protection against threats of other kinds has become a heightened concern. Principal among those concerns is security of the pilots and cockpit against firearms. A need exists for lightweight materials, for use in cockpit doors, that are resistant to penetration by handgun ammunition, and which also maintain current standards of fire resistance.

[0003] Fire resistant materials for aircraft interiors have been described in USP's 4,780,359; 5,175,198; 5,714,419 and 5,972,512. USP 6,044,605 describes a door construction that, "...can be made with fire-resistant and ballistic-resistant materials..." .

[0004] USP 3,934,066 describes a fire-retardant laminate system suitable for application to a combustible or heat sensitive substrate comprising a flexible protective layer, and an intumescent layer comprising a porous cellulosic sheet material impregnated with an intumescent composition. The flexible protective layer may be a metal foil.

[0005] Materials possessing both fire resistance and ballistic resistance have been described in USP's 4,822,439; 4,842,923; 4,929,651; 5,167,876; 5,215,813 and 5,480,706.

[0006] USP's 4,822,439 and 4,929,651 describe composites comprising about 60% to about 75% by weight of woven magnesia aluminosilicate fiberglass roving impregnated with calcium hydroxide and an isophthalic thermoset polyester.

[0007] USP's 4,842,923 and 5,167,876, describe composites comprising a plurality of layers of a balanced interlaced magnesia aluminosilicate glass fiber fabric in a matrix of a cured phenol formaldahyde resin having an areal density of at least 12.2 kg/m^2 (2.5 pounds per square foot).

[0008] USP 5,167,876, describes a composite comprising two or more layers, at least one of the layers being a network of fibers in a matrix and at least one of the layers being a fire retardant layer having endothermic properties on exposure to heat.

[0009] USP 5,480,706, describes a composite comprising a plurality of alternating first and second plies wherein the first ply comprises a network of high strength flammable fibers in a first matrix and the second ply comprises a network of fire resistant organic or inorganic fibers in a fire resistant matrix.

[0010] US 4,309,487 discloses a laminated armor structure comprising an olefin polymer film.

[0011] DE 2642883 is directed towards projectile-stopping composite materials.

[0012] GB 2232063 discloses a shield for protection against projectiles comprising a plurality of parallel layers of textile fabric and at least one layer comprising fibres that are perpendicular to the plurality of parallel layers of textile fabric.

[0013] GB 2347112 discloses an anti-ballistic panel comprising a laminated structure, for use in the construction of vehicle bodies.

[0014] US 4,822,647 is directed towards a bullet resistant panel defined by an assembly including plural layers of impact resistant fabric and a layer of insulating foam.

[0015] Each of the composite articles cited above represented progress toward the goals to which it was directed. However, none described the specific constructions of the present invention and none satisfied all of the needs met by this invention.

[0016] These earlier composite articles had the principal disadvantage of being largely comprised of relatively dense inorganic materials such as glass fibers. Such materials are not ideal for aircraft interiors where excess weight translates into unnecessary and costly fuel consumption. On the other hand, composite densities can be too low and take up excessive space. A need exists for composite materials exhibiting strength, toughness, ballistic resistance, and fire resistance combined with useful density.

SUMMARY OF THE INVENTION

[0017] The invention provides composite articles exhibiting strength, toughness, ballistic resistance, fire resistance and useful density in heretofore unknown combination, as defined in claim 1.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The invention provides composites exhibiting strength, toughness, ballistic resistance, fire resistance and low density in heretofore unknown combination.

[0019] The flexural modulus (modulus of elasticity in bending) and the flexural strength at yield of a composite may be measured by American Society of Testing and Materials (ASTM) Standard Test Method ASTM D790-00.

[0020] Title 14 USC §25.853 sets forth the flammability standards for aircraft compartment interiors. Materials for interior partitions must meet the test requirements prescribed in Appendix F, Parts I, IV and V.

[0021] 14 USC §25.853, Appendix F, Part I(a)1(i) specifies that partition materials must be self-extinguishing when tested vertically. Specimens to be tested must be at least 5 cm (2 inches) wide, 30 cm (12 inches) long and no thicker than the minimum thickness to be qualified for use in aircraft. A minimum of three specimens must be tested and results averaged. The specimen is exposed to the flame of a Bunsen or Tirrill burner with a minimum flame temperature of 843°C (1550°F). The flame is applied to the centerline of the lower edge of the specimen for 60 seconds and then removed. Average flame time after removal of the flame source may not exceed 15 seconds. The average burn length may not exceed 15 cm (6 inches). Drippings from the test specimen, if any, may not continue to flame for more than an average of 3 seconds after falling.

[0022] 14 USC §25.853, Appendix F, Part IV specifies the maximum heat release rate from cabin materials exposed to radiant heat in a specially designed test chamber. Specimens are exposed to a radiant heat source adjusted to produce on the specimen, a total heat flux of 3.4 Watts/cm^2 over a five minute test duration. Test specimens are 14.9 cm x 14.9 cm (5.91 in x 5.91 in) and of the same thickness as to be used in aircraft. The specimen is tested with the exposed surface vertical. Combustion products leaving the test chamber are monitored to calculate the heat release rate. The total positive heat release over the first two minutes of exposure for each of the three or more samples are averaged, and the peak heat release rates for the samples are averaged. The average peak heat release rate must not exceed 65 kW/m^2. If melting, sagging, delamination, or other behavior that affects the exposed surface area or the mode of burning occurs, these behaviors must be reported together with the time at which such behaviors were observed.

[0023] 14 USC §25.853, Appendix F, Part V specifies the maximum smoke emission characteristics of cabin materials and refers to ASTM F814-83 for details of the test procedure. A minimum of three specimens must be tested and results averaged. Test specimens 7.62 x 7.62 cm (3 x 3 inches) are mounted in a vertical orientation within a specially designed chamber. An electrically heated radiant-energy source produces an irradiance level of 2.5 W/cm^2 (2.2 BTU/ s-ft^2) averaged over the 3.81 cm (1.5 inch) diameter central area of the specimen. A six-tube burner is used to apply a row of equidistant flames across the lower edge of the exposed specimen area. The specific optical smoke density (Ds) obtained after 1.5 minutes and 4 minutes, as well as the maximum value of optical smoke density DsMax and the DsMax time are recorded. The average DsMax must not exceed 200.

[0024] The V0 velocity of a composite is the maximum velocity at which a specified projectile will not penetrate the composite. The V0 velocity of a composite of the invention is determined by the test procedures of United States FAA AC 25.795.2, 10 Jan. 2002, using .44 Magnum JHP bullets of 15.6 g (240 grains) mass and using 9 mm FMJ RN bullets of 8.0 g (124 grains) mass.

[0025] The velocity of the projectile is measured by lumiline screens along the path of the projectile. The test panel is mounted normal to the path of the projectile for four shots and also 30° off the normal for two shots with each projectile. The V0 velocity is determined by varying the propellant charge so as to cause complete and partial penetrations of the test panel at each impingement angle. The V0 velocity is the highest partial penetration velocity. A composite may have a V0 velocity at least about 427 m/s (1430 ft/sec) when tested using .44 Magnum JHP bullets of 15.6 g (240 grains) mass and when using 9 mm FMJ RN bullets of 8.0g (124 grains) mass.

[0026] A composite article of the invention is comprised of a plurality of plies bonded together, wherein a first ply is comprised of a metal foil, a second ply is comprised of a fire retardant bonding material and a third ply is comprised of a plurality of layers, each of said layers comprising a network of flammable polymeric fibers in a matrix, said polymeric fibers having a tenacity of at least about 17 g/denier, a tensile modulus of at least about 500 g/denier and an energy-to-break of at least about 20 Joules/g.

[0027] In another embodiment, a composite article of the invention is comprised of a plurality of plies bonded together, wherein a first ply is comprised of a metal foil, a second ply is an intumescent resinous composition, a third ply is comprised of a fire retardant bonding material, and a fourth ply is comprised of a plurality of layers, each of said layers comprising a network of flammable polymeric fibers in a matrix, said polymeric fibers having a tenacity of at least about 17 g/denier, a tensile modulus of at least about 500 g/denier and an energy-to-break of at least about 20 Joules/g.

[0028] Preferably, a composite article of the invention possesses a symmetric ply structure with the central ply being comprised of the network of flammable polymeric fibers in a matrix. In one preferred embodiment, the composite article is comprised of five plies bonded together, wherein the first and fifth plies are comprised of a metal foil, the second and fourth plies are comprised of a fire retardant bonding material and the central third ply is comprised of a network of flammable polymeric fibers in a matrix, said polymeric fibers having a tenacity of at least about 17 g/denier, a tensile modulus of at least about 500 g/denier and an energy-to-break of at least about 20 Joules/g.

[0029] In another preferred embodiment, the composite article is comprised of seven plies bonded together, wherein the first and seventh plies are comprised of a metal foil, the second and sixth plies are an intumescent resinous composition, the third and fifth plies are a fire retardant bonding material and the central fourth ply is comprised of a network of flammable polymeric fibers in a matrix, said polymeric fibers having a tenacity of at least about 17 g/denier, a tensile modulus of at least about 500 g/denier and an energy-to-break of at least about 20 Joules/g.

[0030] The plies in each embodiment are assembled and bonded together. Preferably the plies are bonded under heat and pressure. Preferably, the bonding is conducted at temperature of about 100°C to about 150°C at a pressure of about 103 kPa (15 psi) to about 34,475 kPa (5,000 psi) for a time sufficient to bond the plies. More preferably, the bonding is conducted at a temperature of about 120°C to about 130°C and at a pressure of about 345 kPa (50 psi) to about 1,380 kPa (200 psi), for a time period of about 30 minutes.

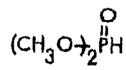
[0031] Preferably, the metal foil in each embodiment is aluminum having a thickness from about 12.7 micrometers (0.0005 inch) to about 127 micrometers (0.005 inches). More preferably, the metal foil is aluminum having a thickness from about 25.4 micrometers (0.001 inch) to about 76.2 micrometers (0.003 inch).

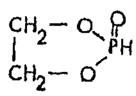
[0032] The fire retardant bonding material is comprised of at least 10% by weight of a polymeric material selected from the group consisting of thermoplastics and thermosets. Thermoplastic polymers useful in the bonding material of the invention include, but are not restricted to: polyolefins, polydienes, polyesters, polyamides, vinyl polymers, ionomers, acrylics, acrylates, polysulfones, polyphenylene oxide, acetals, silicones, thermoplastic polyurethanes, thermoplastic polyimides, polyketones, and copolymers and halogenated derivatives thereof. Useful thermoset polymers include, but are not restricted to: phenolic polymers, melamine polymers, epoxies, silicones, unsaturated polyesters, and thermosetting polyurethanes.

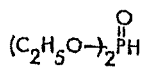
[0033] The polymeric portion of the fire retardant bonding material also includes a fire retardant additive.

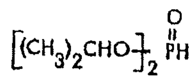
[0034] The fire retardant additive may be organic, inorganic, or organometallic and is selected from the following:

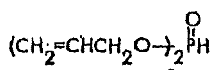
the following **P-H Functional** compounds

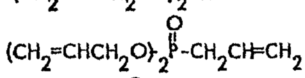


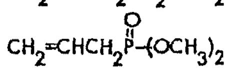


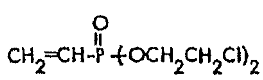


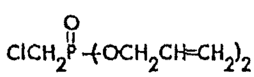


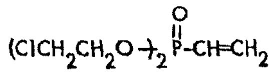


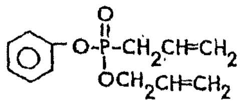




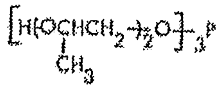


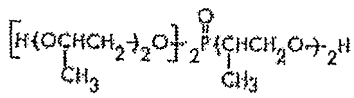


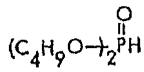


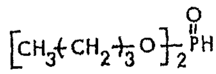


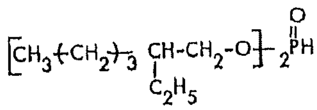
the following **-OH Functional** compounds

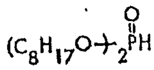


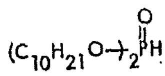


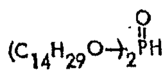


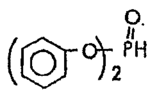


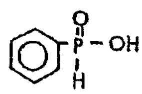


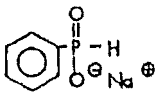












the following **$CH_2{=}CH$- Functional** compounds

$$(CH_2{=}CHCH_2O\text{-})_3P$$

$$(CH_2{=}CHCH_2O\text{-})_3P{=}O$$

$$HOCH_2\overset{O}{\overset{\|}{P}}\text{-}[O(CH_2CH_2O\text{-})_3H]_2$$

$$ClCH_2\overset{O}{\overset{\|}{P}}\text{-}[(OCH_2\underset{CH_3}{CH}\text{-})_nOH]_2$$

$$(CH_3CH_2O\text{-})_2\overset{O}{\overset{\|}{P}}\text{-}CH_2N\text{-}(CH_2CH_2OH)_2$$

$$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}CH_2CH_2OH$$

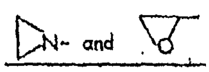
$$(CH_3O)_2\overset{O}{\overset{\|}{P}}\text{-}CH_2CH_2\overset{O}{\overset{\|}{C}}\overset{H}{N}\text{-}CH_2OH$$

$$(BrCH_2CHBrCH_2O)_2\overset{O}{\overset{\|}{P}}\text{-}\overset{H}{N}\text{-}CH_2OH$$

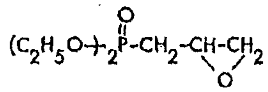
$$(BrCH_2\text{-}CHBr\text{-}CH_2O)_2\overset{O}{\overset{\|}{P}}\text{-}N(CH_2OH)_2$$

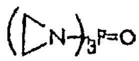
$$(BrCH_2CHBrCH_2O)_2\overset{O}{\overset{\|}{P}}\text{-}O\text{-}CH_2CH_2\,O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{\underset{C=CH_2}{CH_3}}{C}{=}CH_2$$

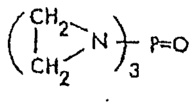
the following



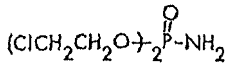
Functional compounds

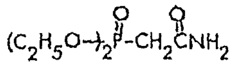


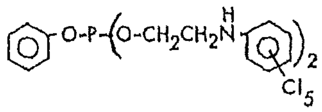


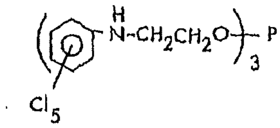


the following **-NH Functional** compounds





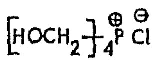




the following

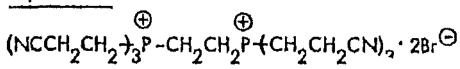
$\overset{\oplus}{P}-CH_2OH$

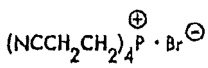
Functional compounds

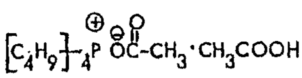


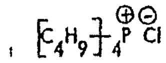
the following ⊕**P{CH$_2$OH)$_4$A**⊖ compounds

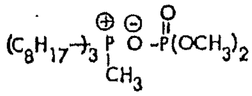
$R_4P^{\oplus}$ Salts











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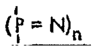
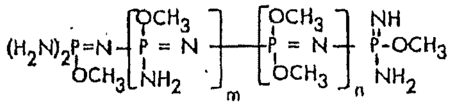
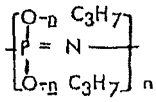
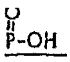


Polymers compounds

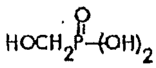


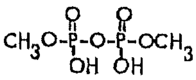


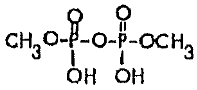
the following

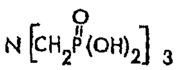


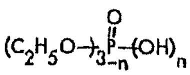
Functional compounds



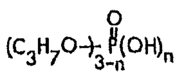








n = 1 to 2



n = 1 to 2

$$BrCH_2CHBrCH_2O\text{-}\overset{O}{\overset{\|}{P}}\text{-}(OH)_2$$
(and $NH_4^{\oplus}$ SALT)

$$(BrCH_2CHBrCH_2O)_2\overset{O}{\overset{\|}{P}}\text{-}OH$$
(and $NH_4^{\oplus}$ SALT)

$$(C_4H_9O)_{3-n}\overset{O}{\overset{\|}{P}}(OH)_n$$

n = 1 to 2

$$(C_4H_9O)_2\overset{O}{\overset{\|}{P}}OH$$

$$(C_4H_9O)_{3-n}\overset{O}{\overset{\|}{P}}(OH)_n$$

n = 1 to 2

$$(C_4H_9O)_{3-n}\overset{O}{\overset{\|}{P}}(OH)_n$$

n = 1 to 2

$$(C_5H_{11}O)_{3-n}\overset{O}{\overset{\|}{P}}(OH)_n$$

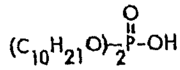
n = 1 to 2

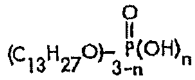
$$(C_8H_{17}O)_2\overset{O}{\overset{\|}{P}}OH$$

$$\left[C_8H_{17}O\text{-}\overset{O}{\overset{\|}{\underset{OH}{\underset{|}{P}}}}\text{-}\right]_2 O$$

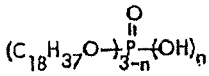
$$(C_8H_{17}O)_{3-n}\overset{O}{\overset{\|}{P}}(OH)_n$$

n = 1 to 2

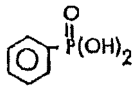


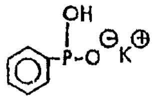


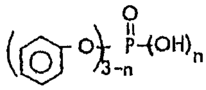
n = 1 to 2



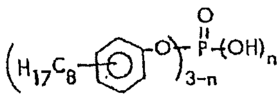
n = 1 to 2





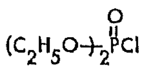


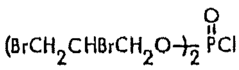
n = 1 to 2

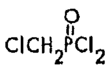


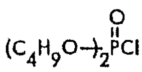
n = 1 to 2

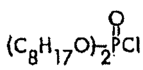
the following **P-Cl Functional** compounds

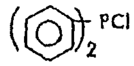


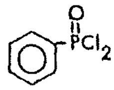








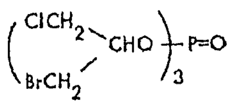




the following **P + S Compounds Functional**

$$(CH_3)_2P-S-S-P(CH_3)_2$$

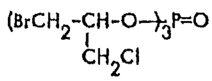
the following **P + Br Compounds**

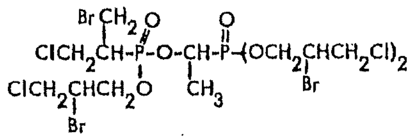


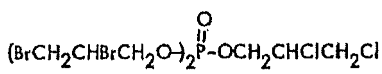
$$(BrCH_2CHBrCH_2O)_3P{=}O$$

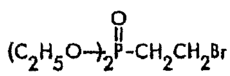
$$(XCH_2CHXCH_2O)_3P{=}O$$

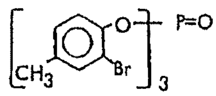
$X = Cl, Br$

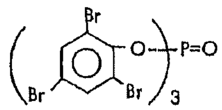












the following **P + Cl Compounds**

$$(ClCH_2CH_2O)_3P$$

$$[(ClCH_2)_2CHO]_3P{=}O$$

$$(ClCH_2CHClCH_2O)_3P{=}O$$

$$(ClCH_2CH_2CH_2O)_3P{=}O$$

$$(ClCH_2CH(CH_3){-}O)_3P{=}O$$

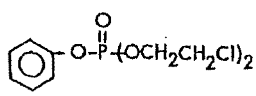
$$(CH_3CHClCH_2O)_3P{=}O$$

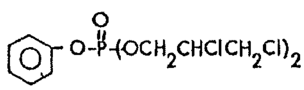
$$C_8H_{17}O{-}P(=O)(OCH_2CH_2Cl)_2$$

$$ClCH_2CH_2P(=O)(OCH_2CH_2Cl)_2$$

$$(ClCH_2)_2C[CH_2OP(=O)(OCH_2CH_2Cl)_2]_2$$

$$(ClCH_2CH_2O)_2P(=O){-}O{-}CH(CH_3){-}P(=O)(OC_2H_4Cl){-}OCH(CH_3){-}P(=O)(OCH_2CH_2Cl)_2$$





the following **P (Phosphites)**

$$(CH_3O)_3P$$

$(CH_3CH_2O)_3P$

$[(CH_3)_2CHO]_3P$

$[CH_3(CH_2)_3O]_3P$

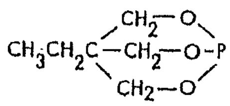
$(C_8H_{17}O)_3P$

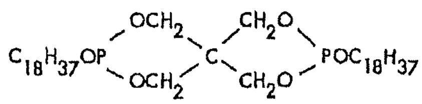
$[CH_3(CH_2)_3CH(C_2H_5)-CH_2O]_3P$

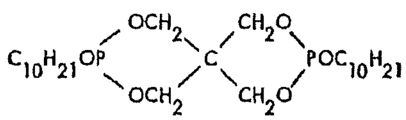
$(C_{12}H_{25}O)_3P$

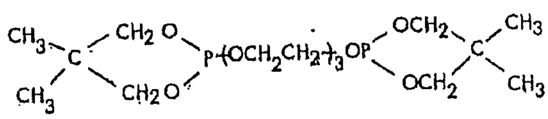
$(C_{18}H_{37}O)_3P$

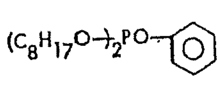
$(C_{18}H_{37}O)_3P$

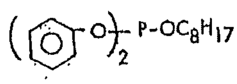


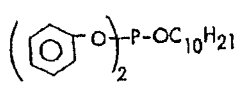


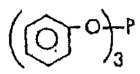


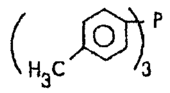


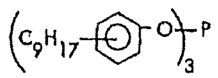












the following **P (Phosphates)**

$$(CH_3O-)_3P=O$$

$(C_2H_5O)_3P=O$

$$(C_2H_5O-)_3P=O$$

$$(C_4H_9O-)_3P=O$$

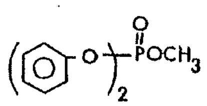
$$(C_8H_{17}O-)_3P=O$$

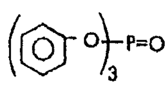
$$(CH_3-(CH_2-)_3\underset{\displaystyle C_2H_5}{\underset{|}{C}}H-CH_3O-)_3P=O$$

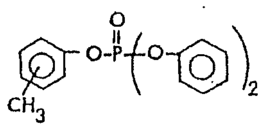
$$(C_8H_{17}O-)_3P=O$$

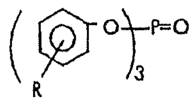
$$(CH_3(CH_2)_3\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}HCH_2O-)_3P=O$$

$$(C_4H_9O-CH_2CH_2O-)_3P=O$$

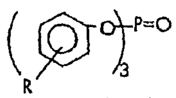




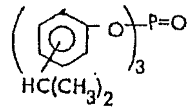


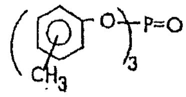


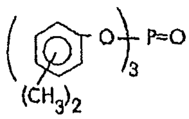
R = H, CH_3

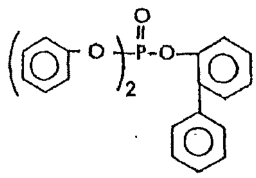


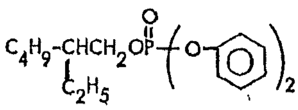
R=H, $(CH_3)_2CH$

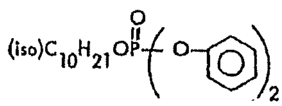




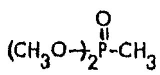


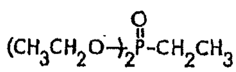


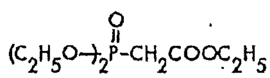




the following **P (Phosphonates)**





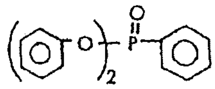


$(CH_3O)_2P(=O)-CH_2CO_2CH_3$

$(C_2H_5O)_2P(=O)-CH_2CN$

$[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_2P(=O)-CH_2CH(C_2H_5)(CH_2)_3CH_3$

$[CH_3(CH_2)_3O]_2P(=O)-(CH_2)_3CH_3$

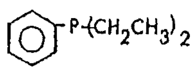


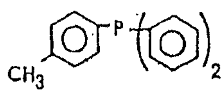
the following **P (Miscellaneous)**

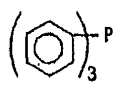
$(C_2H_5O)_{1.5}P(=O)(ONH_4)_{1.5}$

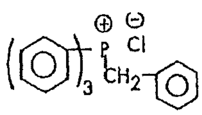
$(n\text{-}C_4H_9)_3P=O$

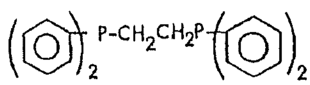
$(n\text{-}C_8H_{17})_3P=O$

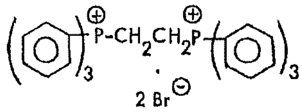


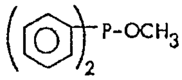


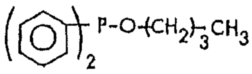


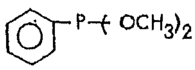


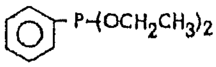


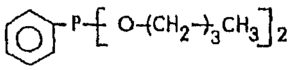


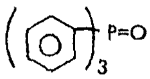












the following **P + S Compounds**

$(C_{12}H_{25}S)_3P$

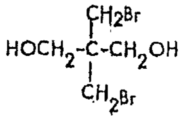
$(CH_3CH_2O)_3P{=}S$

$[CH_3(CH_2)_3O]_3P{=}S$

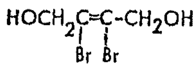
$(C_8H_{17}O)_3P{=}S$

the following **Bromo - Compounds :-OH Functional** compounds

$(BrCH_2)_3C\text{-}OH$

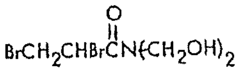


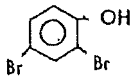
$BrCH{=}CB_r\text{-}CH_2OH$

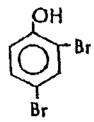


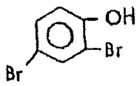
$BrCH_2CH_2OH$

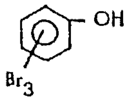
$BrCH_2CHBrCH_2OH$

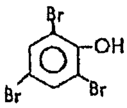


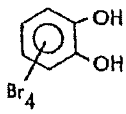


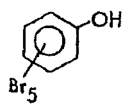


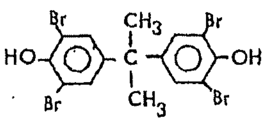


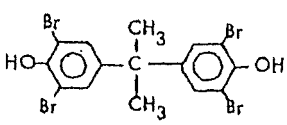


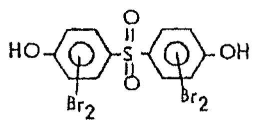


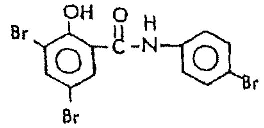


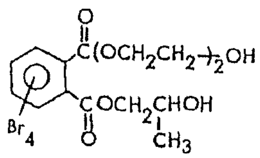


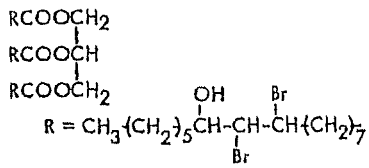


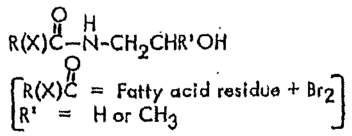


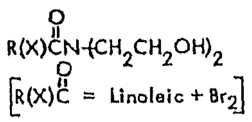


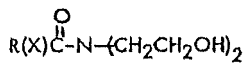


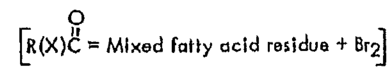




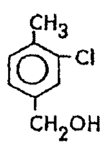


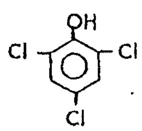


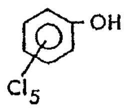


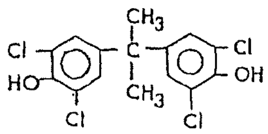


the following **Chloro- Compounds: -OH Functional** compounds

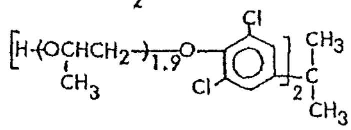


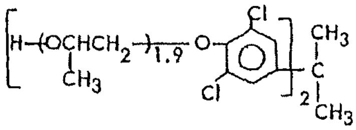


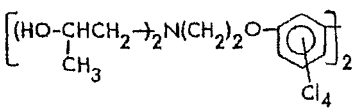


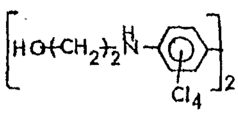


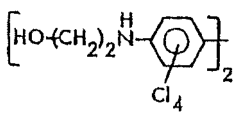
Product of Cl_2 and

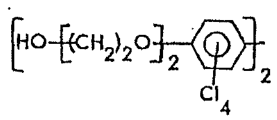






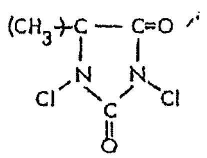


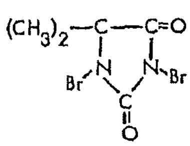


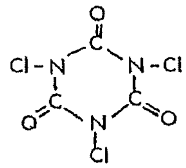


the following **-C≡C - Functional** compounds **$Cl\text{-}CH_2\text{-}C{\equiv}C\text{-}CH_2Cl$**

the following **N-Halogen Functional** compounds

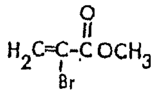


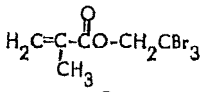


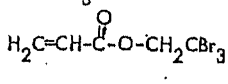


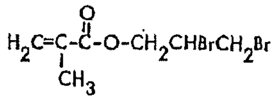
the following **$H_2C=C$ - Functional** compounds **$CH_2=CH-Br$**

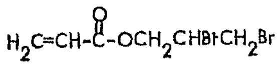
$CH_2=CH-CH_2Br$

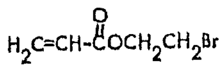


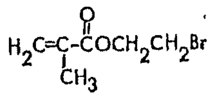


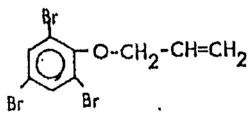


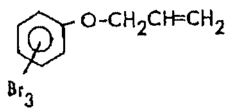


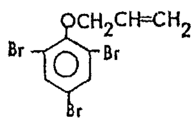


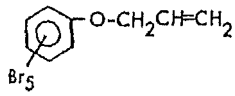


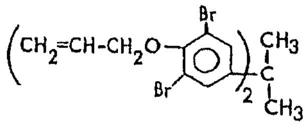


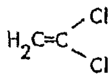






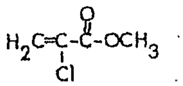


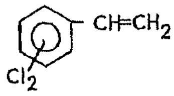


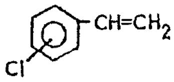


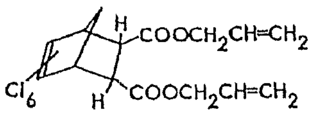
CH_2=CCl_2

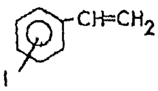
CH_2=CH-CH_2Cl





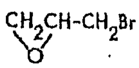


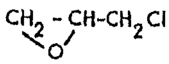


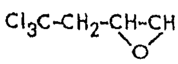


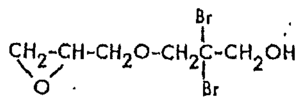
the following

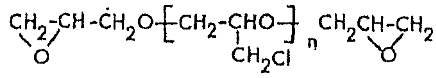
Functional compounds



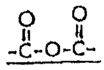




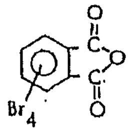


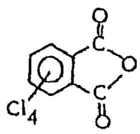


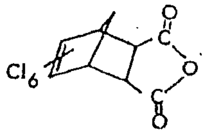
the following

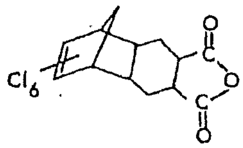


Functional compounds

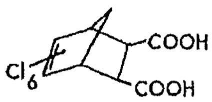


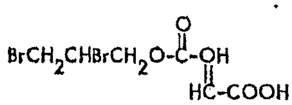






the following **-COOH Functional** compounds



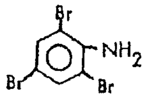


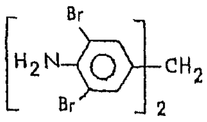
(And NH_4^+ Salt)

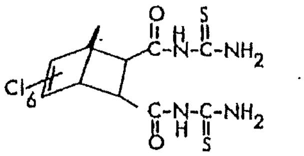
the following **-CHO Functional** compounds **$BrCH_2CHBr$-CHO**

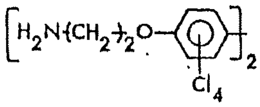
Cl_3C-CHO

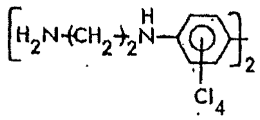
the following **-NH_2 Functional** compounds

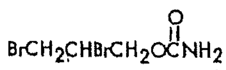












THE FOLLOWING **NON-FUNCTIONAL HALOGEN COMPOUNDS**
Bromo-Compounds

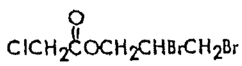
$BrCH_2Cl$

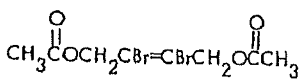
$Br_2CH\text{-}CHBr_2$

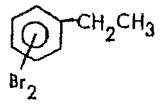
$BrCH_2CH_2CHCl$

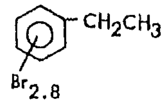
$BrCH_2CHBrCHBrCH_2Br$

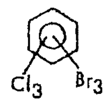
$(BrCH_2CHBrCH_2O)_2CH_2$

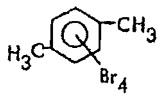


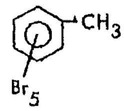


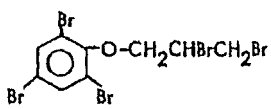


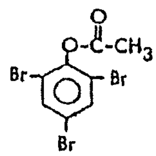


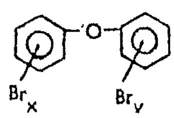




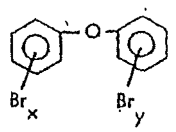




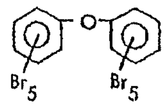


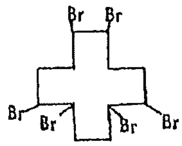


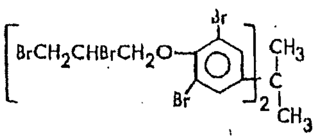
$x + y = 5$

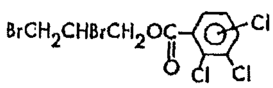


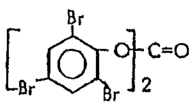
x + y = 8

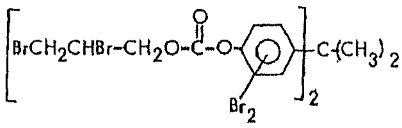


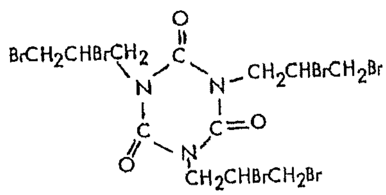


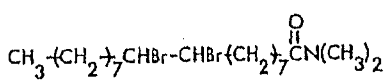










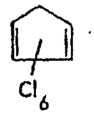


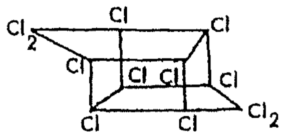
Chloro-Compounds

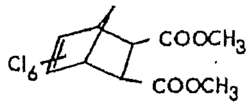
$Cl_3C\text{-}CCl_3$

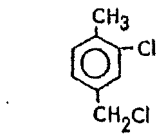
$ClCH_2CHClCH_2Cl$

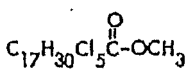
$Cl_2C{=}CCl{-}CCl{=}CCl_2$



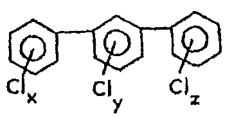


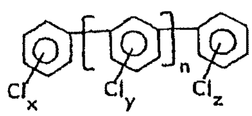




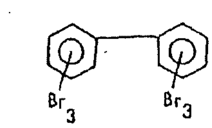


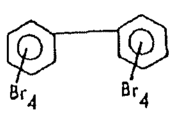
Chloro-Tri (and higher) Phenyls

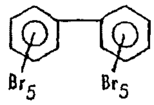


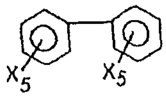


Bromo- and Chloro-Biphenyls

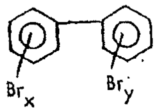




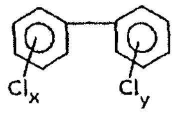




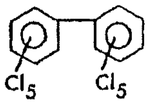
X_6 = Cl
X_4 = Br



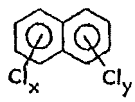
x + y = 8

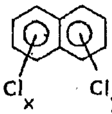


(x + y = 1 - 10)



Chloro- Naphthalenes





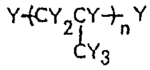
HALOGENATED PARAFFINES

$$CY_3\text{-}(CY_2)_n\text{-}CY_3$$

Y = Br, H

$$CY_3\text{-}(CY_2)_n\text{-}CY_3$$

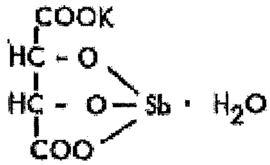
Y = H, Cl

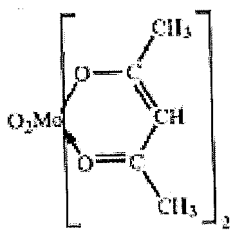


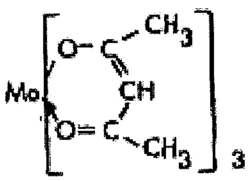
Y = H, Cl

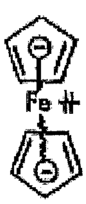
suitable inorganic fire retardant additives include: antimony oxide (Sb_2O3), antimony sulfides (Sb_2OS_3, Sb_2S_3, Sb_2S_4), antimony halides ($SbCl_3$, $SbCl_5$, $SbBr_3$, $SbBr_5$), sodium or potassium antimonite, e.g., ($NaSbO_3$), ammonium, sodium or potassium phosphates, e.g., ($(NH_4)_3PO_4$, $(NH_4)_2HPO_4$, $(NH_4)H_2PO_4$, $(NH_4PO_3)_x$), phosphorus halides (PCl_3, PCl_5, $POCl_3$), phosphonitrilic chloride $(PNCl_2)_x$, phosphorus pentasulfide (P_2S_5), sodium borates ($Na_2O(B_2O_3)_{3.5}\cdot 4\ H_2O$, $Na_2B_4O_7\cdot 10\ H_2O$), sodium, potassium or ammonium tetrafluoroborate, e.g. ($NaBF_4$), calcium or barium borates, e.g., ($Ca(BO_2)_2$, $Ca_3(BO_3)_2$), lithium, sodium or potassium tetraborate, e.g. (LiB_4O_7), boric acid (H_3BO_3), trimethoxyborozine ($(CH_3OBO)_3$), aluminum oxide hydrates ($Al_2O_3\cdot 3\ H_2O$, $Al(OH)_3$), aluminophosphate hydrates ($Al_2O_3\cdot(AlPO_4)_x\cdot(H_2O)_y$), sodium silicates ($(Na_2O)_nSiO_2)_m$), ammonium bromide ($NH_4Br$), ammonium sulfate ($(NH_4)_2SO_4$), lithium silicates ($LiO_2(SiO_2)_{5.9}$, $Li_2O(Na_2O)_n(SiO_2)_m$)), molybdenum oxide (MoO_3), ammonium paramolybdate ($(NH_4)_6Mo_7O_{24}(H_2O)_x$), molybdenum sulfide ($MoS_2$), and sulfamide ($(NH_2)_2SO_2$).

suitable organometallic fire retardant additives include the following:









[0035] Intrinsically fire retardant polymers useful in the fire retardant bonding material chlorinated polyethylene, polyvinyl chloride, poly(1,1-dichloroethylene), poly(chlorotrifluoroethylene), poly(1,1-dichloro-2-fluoroethylene), poly(1,2-dichloro-1,2-difluoroethylene), poly(1,1-difluoroethylene), poly(1,2 difluoroethylene), poly(tetrafluoroethylene), poly(trifluoroethylene), poly((pentafluoroethyl)ethylene), poly(tetradecafluoropentylethylene), poly(hexafluoropropylene), poly(2,3,3,3-tetrafluoropropylene), poly(3,3,3-trifluoropropylene), poly(heptafluoropropyl)ethylene), poly(vinylidene fluoride), and poly(tribromostyrol), mixtures thereof, and copolymers of the antecedent monomers comprising these polymers and melamine-formaldahyde, urea -formaldahyde, and phenol-formaldahyde.

[0036] Preferably the fire retardant bonding material is comprised of a blend of antimony oxide (Sb_2O_3), decabromodiphenyl ether and polychlorinated paraffin wax in a polyacrylate resin binder designated BOSTIK®14-576-3 (Bostik Findley, Inc.).

[0037] The non-polymeric portion of the fire retardant bonding material may be comprised of an intumescent composition. Intumescent compositions act by forming, under the influence of heat, an expanded insulating layer of fire resistant material. The intumescent material may also undergo an endothermic decomposition.

[0038] An intumescent composition swells to produce a char more than five times its original thickness. The expanded material shields a substrate from oxygen and/or from overheating and thereby prevents or delays the spread of flame. Intumescent systems typically consist of a polymer, a char or carbon skeleton-forming substance ("carbonific"), an expanding agent ("spumific") and an acid forming substance. As carbonifics, organic polyhydroxy compounds such as pentaerythritol, dipentaerythritol, tripentaerythritol, starch and sugars have been employed. Examples of spumifics are nitrogen-containing compounds such as melamine, melamine salts, melamine derivatives, urea, dicyandiamide and guanidine. The spumific effects the formation of an intumescent layer by emission of an inert gas. As acid forming substances usually an aminophosphate, ammonium phosphates, amine phosphates, ammonium polyphosphates, and melamine phosphate have been employed.

[0039] Intumescent compositions useful in the present invention have been described, for example, in USP's 6,309,746 B1; 6,228,914 B1; 5,962,603; 5,759,692; 5,708,065; 5,591,791; 5,356,568; 5,225,464; 5,185,103; 5,130,349; 4,857,364; 4,442,157; 4,542,170; 4,380,593; 4,198,328 and 3,849,178.

[0040] In a preferred embodiment, a composite article of the invention is comprised of at least one ply of an intumescent resinous composition. A preferred intumescent resinous composition is a mixture of Borden Chemical phenolic resin FIRE PRF2-1000 and about 8 to about 18 wt% of a material comprised of melamine pyrophosphate ($C_3H_6N_6 \cdot H_4P_2O_7$) and bis(melamine pyrophosphoric) acid ($C_6H_{12}N_{12} \cdot H_4P_4O_7$) sold by Broadview Technologies, Inc., under the designation of MAXICHAR®.

[0041] Preferably, the intumescent resinous composition is additionally comprised of about 2 to about 35 wt% of glass bubbles such as the soda-lime borosilicate glass bubbles sold by Minnesota Mining and Manufacturing Co. under the designation 3M® SCOTCHLITE® glass bubbles. Most preferably, the glass bubbles are of a size such that no more than 5 wt.% are retained on a Number 80 U.S. Standard Sieve (177 micron).

[0042] It is preferred that at least one ply of a composite article of the invention is comprised of a plurality of layers, each of said layers comprising a network of flammable polymeric fibers in a matrix, said polymeric fibers having a tenacity of at least about 25 g/denier, a tensile modulus of at least about 900 g/denier and an energy-to-break of at least about 25 Joules/g.

[0043] For the purposes of the present invention, a fiber is an elongate body the length dimension of which is much greater that the transverse dimensions of width and thickness. Accordingly, the term fiber includes filament, ribbon, strip, and the like having regular or irregular cross-section. A yarn is a continuous strand comprised of many fibers or filaments.

[0044] As used herein, "fiber network" denotes a plurality of fibers arranged into a predetermined configuration, or a plurality of fibers grouped together to form a twisted or untwisted yarn, which yarns are arranged into a predetermined configuration. The fiber network can have various configurations. For example, the fibers or yarn may be formed as a felt or other nonwoven, knitted or woven into a network by any conventional techniques. According to a preferred network configuration, the fibers in a layer are unidirectionally aligned so that they are substantially parallel to each other along a common fiber direction. Successive layers of such unidirectionally aligned fibers are preferably rotated with respect to the previous layer.

[0045] Flammable fibers are those that will support combustion. Flammable fibers include unmodified polyolefins, polyesters, polyvinyl alcohol, and polyacrylonitrile.

[0046] Most preferably, the fiber network layers of the composite are arranged with the fiber direction of the unidirectional fibers of each network layer rotated with respect to the fiber direction of the unidirectional fiber of the adjacent layers. An example is a five layer ply with the second, third, fourth and fifth layers rotated +45°, -45°, 90° and 0° with respect to the first layer. A particularly preferred example is a fifty-layer ply with alternate layers aligned at 0° and 90° to each other.

[0047] Most preferably the flammable fibers comprising a composite of the invention are high strength polyethylene fibers. High strength polyethylene fibers for use in this invention are those having a tenacity equal to or greater than about 17 g/d, initial tensile modulus equal to or greater than about 500 g/d and an energy-to-break equal to or greater than about 20 J/g. For the purposes of this invention, the fiber tenacity, initial tensile modulus (modulus of elasticity) and energy-to break are measured in yarn form by ASTM D2256. Preferred fibers are those having a tenacity equal to or greater than about 25 g/d, initial tensile modulus equal to or greater than about 900 g/d and an energy-to-break equal to or greater than about 25 J/g. Particularly preferred fibers are those having a tenacity equal to or greater than about 30 g/d, initial tensile modulus equal to or greater than about 1200 g/d, and an energy-to-break equal to or greater than about 30 J/g. Most preferred fibers are those having a tenacity equal to or greater than about 30 g/d, initial tensile modulus equal to or greater than about 1200 g/d, and an energy-to-break equal to or greater than about 40 J/g.

[0048] Such high strength polyethylene fibers may be grown in solution as described in USP's 4,137,394 or 4,356,138 or spun from a solution to form a gel structure, as described in German Off. No. 3,004, 699 and GB No. 2051667, and especially as described in USP 4,413,110. The polyethylene fibers may also be produced by a rolling and drawing process as described in USP 5,702,657 and sold under the name TENSYLON® by ITS Industries Inc. As used herein, the term polyethylene means a predominantly linear polyethylene material that may contain minor amounts of chain branching or comonomers not exceeding 5 modifying units per 100 main chain carbon atoms, and that may also contain admixed therewith not more than about 50 wt % of one or more polymeric additives such as alkene-I-polymers, in particular low density polyethylene, polypropylene or polybutylene, copolymers containing mono-olefins as primary monomers, oxidized polyolefins, graft polyolefin copolymers and polyoxymethylenes, or low molecular weight additives such as antioxidants, lubricants, ultraviolet screening agents and colorants.

[0049] Surprisingly, the composite articles of the invention meet the stringent fire resistant requirements for aircraft interiors despite the fact that the major portion is comprised of flammable fiber networks shielded by relatively thin fire retardant surface layers. Without being held to a particular theory of why the invention works, it is believed that the fiber network layers and the fire retardant surface layers work cooperatively to retard the propagation of a flame source. The outer metal foil and fire retardant bonding material block oxygen and provide an initial delay to propagation of high temperatures to the interior of the composite. When a high temperature front finally penetrates the outer layers of the composite, the flammable fibers shrink away from the heat source, creating a void space and delaying further propagation. In embodiments where an intumescent resinous composition lies between the fiber network layers and the composite surface, this delay is further increased. The total effect is a highly effective fire retardant composite meeting the requirements for aircraft interiors with a very wide margin of safety.

[0050] The following examples are presented to provide a more complete understanding of the invention. The specific techniques, conditions, materials, proportions and reported data are set forth to illustrate the principles of the invention and should not be construed as limiting the scope of the invention. In particular, the techniques described were for the preparation of test samples and are readily extended to implementation on a continuous production line.

EXAMPLES

Comparative Example 1

[0051] A nine-ply composite article was prepared having a symmetrical ply construction as follows:

1st and 9th plies: type 302 stainless steel foil, 0.0254 mm (0.001 inch) thick;
2nd and 8th plies: intumescent resinous composition;
3rd and 7th plies: glass fabric impregnated with phenolic resin;
4th and 6th plies: fire retardant pressure sensitive film adhesive; and
5th ply: 50 layers of unidirectional polyethylene fiber networks in an epoxy vinyl ester matrix.

[0052] The intumescent resinous composition comprising the 2nd and 8th plies was a sheet material prepared as follows: A mixture was prepared consisting of 60.9 wt.% of a two-part formaldehyde-furfural-resorcinol-phenol monomer (Borden Durite FIRE PRF2-1000; Part A-100 pph, Part B-24 pph), 9.1 wt.% of an intumescent additive comprising melamine pyrophosphate ($C_3H_6N_6 \cdot H_4P_2O_7$) and bis(melamine pyrophosphoric) acid ($C_6H_{12}N_{12} \cdot H_4P_4O_7$) (Broadview Technologies MAXICHAR®) and 30 wt.% of glass bubbles (3M Type K1). The mixture was evenly spread to a thickness of 0.51 mm (0.020 inch) on a silicone release paper with another release paper placed on top. The mixture was cured into a solid sheet by heating for 30 minutes at about 93°C (200°F) under slight pressure of about 7 kPa (1 psi) in a press. The edges of the sheet were trimmed to straightness and the sheet was divided into two equal sections to form the 2nd and 8th plies of the composite.

[0053] The impregnated glass fabric comprising the 3rd and 7th plies was a 22 x 21 ends/cm (57 x 54 ends/inch) satin weave E-glass fabric, style 7781, pre-pregged with fire retardant LC 194 phenolic resin (Lewcott Corp.) and having a thickness of about 2.41 mm (0.095 inch).

[0054] The fire-retardant, pressure-sensitive film adhesive forming the 4th and 6th plies was a blend of antimony oxide (Sb_2O_3), decabromodiphenylether and polychlorinated paraffin wax in an acrylate ester resin binder designated BOSTIK®14-576-3 (Bostik Findley, Inc.).

[0055] The central fifth ply consisted of 50 layers of high strength polyethylene fibers, unidirectionally aligned within a layer and arranged with the fibers in adjacent layers oriented at 90° to one another. The polyethylene fibers were of 1100 denier, had a tensile strength of about 3.1 GPa, an initial tensile modulus of about 107 GPa, an elongation-to-break of about 3.3% and were in a matrix comprising an epoxy vinyl ester resin having a tensile modulus of about 3.5 Gpa (500 kpsi). (SPECTRA SHIELD® VE PLUS from Honeywell International Inc.)

[0056] The plies of the composite article were assembled and bonded together in a press under a pressure of 690 kPa (100 psi) at a temperature of 121°C for 30 minutes.

[0057] A test of the composite article conducted according to14 USC §25.853, Appendix F, Part IV, showed an average maximum heat release rate of 11 kW/m^2 compared to a requirement of less than 65 kW/m^2. However, the panel had an areal density of 8.99 kg/m^2 (1.84 lb/ft^2), which was considered excessive.

Comparative Example 2

[0058] A nine-ply composite article was prepared having a symmetrical ply construction identical to that in Comparative Example 1 except for the 2nd and 8th plies. The intumescent resinous composition comprising the 2nd and 8th plies was a sheet material prepared as follows:
The two parts of an intumescent epoxy resin containing melamine pyrophosphate and bis(melamine pyrophosphoric) acid (INTUMAX® EP1115, Broadview Technologies, Inc.) were mixed together and evenly spread to a thickness of 0.51 mm (0.020 inch) on a silicone release paper with another release paper placed on top. No glass bubbles were included in this resin. The mixture was cured into a solid sheet by heating for 30 minutes at about 93°C (200°F) under slight pressure of about 7kPa (1 psi) in a press. The edges of the sheet were trimmed to straightness and the sheet was divided into two equal sections to form the 2nd and 8th plies of the composite.

[0059] The remaining plies of the composite were identical to the corresponding plies described in Comparative Example 1.

[0060] The plies of the composite article were assembled and bonded together in a press under a pressure of 690 kPa (100 psi) at a temperature of 121°C. for 30 minutes.

[0061] A test of the composite article conducted according to 14 USC §25.853, Appendix F, Part IV, showed an average maximum heat release rate of 47 kW/m^2. This was within an acceptable range but poorer than the 11 kW/m^2 for the composite prepared in Comparative Example 1 and containing the glass bubbles. This composite article had an improved areal density of 7.62 kg/m^2 (1.56 lb/ft^2), which was considered to be about at the outer edge of acceptability.

Example 1

[0062] A seven-ply composite article was prepared having a symmetrical ply construction as follows:

1st and 7th plies: aluminum foil, 0.076 mm (0.003 inch) thick;
2nd and 6th plies: intumescent resinous composition;
3rd and 5th plies: fire retardant pressure sensitive film adhesive; and
4th ply: 50 layers of unidirectional polyethylene fiber networks in an epoxy vinyl ester matrix.

The intumescent resinous composition comprising the 2nd and 6th plies was prepared as follows: A mixture was prepared consisting of 95.3 wt.% of a two-part intumescent epoxy resin (INTUMAX® EP1115, Broadview Technologies, Inc.) and 4.7 wt.% of glass bubbles (3M Type K1). The mixture was evenly spread to a thickness of 0.41 mm (0.016 inch) on a silicone release paper with another release paper placed on top. The mixture was cured into a solid sheet by heating for 30 minutes at about 93°C (200°F) under slight pressure of about 7 kPa (1 psi) in a press. The edges of the sheet were trimmed to straightness and the sheet was divided into two equal sections to form the 2nd and 6th plies of the composite.

[0063] The 3rd and 5th plies forming the fire-retardant, pressure-sensitive film adhesive comprised a blend of antimony oxide (Sb_2O_3), decabromo diphenyl ether and polychlorinated paraffin wax in an acrylate ester resin binder designated BOSTIK®14-576-3 (Bostik Findley, Inc.).
The central, fourth ply consisted of 50 layers of high strength polyethylene fibers, unidirectionally aligned within a layer and arranged with the fibers in adjacent layers oriented at 90° to one another. The polyethylene fibers were of 1100 denier, had a tensile strength of about 3.1 GPa an initial tensile modulus of about 107 GPa, an elongation-to-break of about 3.3%, an energy-to-break of about 45 Joules per gram and were in a matrix comprising an epoxy vinyl ester resin having a tensile modulus of about 3.5 Gpa (500 kpsi) (SPECTRA SHIELD® VE PLUS from Honeywell International Inc.).

[0064] The plies of the composite article were assembled and bonded together in a press under a pressure of 690 kPa (100 psi) at a.temperature of 121°C. for 30 minutes.

[0065] This composite article of the invention had an areal density of 5.96 kg/m^2 (1.22 lb/ft^2) which was considered acceptable. The composite was subjected to testing according to 14 USC §25.853, Appendix F, Jan. 1, 2002, and United States United States Federal Aviation Administration Advisory Circular 25.795.2, 10 Jan. 2002, using .44 Magnum JHP bullets of 15.6 g (240 grains) mass and using 9 mm FMJ RN bullets of 8.0 g (124 grains) mass.

[0066] Flexural modulus (modulus of elasticity in bending) and the flexural strength at yield of the composite article was measured by the method of ASTM D790-00. The results of these tests are shown in Table I along with data for other examples and comparative examples. The composite article of Example 1 of the invention (comprising flammable polyethylene fibers) met all Federal Aviation Administration (FAA) requirements.

Example 2

[0067] A seven-ply composite article was prepared in an identical manner and having the same structure as the composite article of Example 1. This composite article had an areal density of 5.82 kg/m^2 (1.19 lb/ft^2), which was considered acceptable. Test results in Table I show that the composite article of Example 2 met all FAA requirements.

Reference **Example 3**

[0068] A seven-ply composite article was prepared having a symmetrical ply construction as follows:

1st and 7th plies: aluminum foil, 0.076 mm (0.003 inch) thick;
2nd and 6th plies: intumescent resinous composition;
3rd and 5th plies: fire retardant pressure sensitive film adhesive; and
4th ply: 50 layers of unidirectional polyethylene fiber networks in a thermoplastic elastomeric matrix (SPECTRA SHIELD® PCR PLUS from Honeywell International Inc.).

[0069] The intumescent resinous composition comprising the 2nd and 6th plies as prepared as follows: A mixture was prepared consisting of 74.2 wt.% of a two-part formaldehyde-furfural-resorcinol-phenol monomer (Borden Durite FIRE PRF2-1000; Part A-100 pph, Part B-24 pph), 12.9 wt.% of an intumescent additive comprising melamine pyrophosphate ($C_3H_6N_6 \cdot H_4P_2O_7$) and bis(melamine pyrophosphoric) acid ($C_6H_{12}N_{12} \cdot H_4P_4O_7$) (Broadview Technologies MAXICHAR®) and 12.9 wt.% of glass bubbles (3M Type K1). The mixture was evenly spread to a thickness of about 0.41 mm (0.016 inch) on a silicone release paper with another release paper placed on top. The mixture was cured into a solid sheet by heating for 30 minutes at about 93°C (200°F) under slight pressure of about 7 kPa (1 psi) in a press. The edges of the sheet were trimmed to straightness and the sheet was divided into two equal sections to form the 2nd and 6th plies of the composite.

[0070] The 3rd and 5th plies comprising the fire-retardant, pressure-sensitive film adhesive comprised a blend of antimony oxide (Sb_2O_3), decabromo diphenyl ether and polychlorinated paraffin wax in a polyacrylate resin binder designated BOSTIK®14-576-3 (Bostik Findley, Inc.).

[0071] The central, fourth ply consisted of 50 layers of high strength polyethylene fibers, unidirectionally aligned within a layer and arranged with the fibers in adjacent layers oriented at 90° to one another. The polyethylene fibers were of 1100 denier, had a tensile strength of about 3.1 Gpa, an initial tensile modulus of about 107 Gpa, an elongation-to-break of about 3.3%, and an energy-to-break of about 45 Joules per gram. The high strength polyethylene fiber networks were in a matrix consisting of a thermoplastic elastomer having a tensile modulus of about 6.9 kPa (100 psi) (SPECTRA SHIELD® PCR PLUS from Honeywell International Inc.).

[0072] The plies of the composite article were assembled and bonded together in a press under a pressure of 690 kPa (100psi) at a temperature of 121°C. for 30 minutes.

[0073] The composite article of the invention had an areal density of 5.82 kg/m^2 (1.19 lb/ft^2) which was, considered acceptable.Test results in Table I show that the composite article of Example 3 met all FAA requirements.

Example 4

[0074] A five-ply composite article was prepared having a symmetrical ply construction as follows:

1st and 5th plies: aluminum foil, 0.025 mm (0.001 inch) thick;
2nd and 4th plies: fire-retardant, pressure-sensitive film adhesive - (BOSTIK®14-576-3); and
3rd ply: 50 layers of unidirectional polyethylene fiber networks in a thermoplastic elastomeric matrix (SPECTRA SHIELD® PCR PLUS from Honeywell International Inc.).

[0075] The plies of the composite article were assembled and bonded together in a press under a pressure of 690 kPa (100 psi) at a temperature of 121°C. for 30 minutes.

[0076] The composite article had a reduced areal density of 4.89 kg/m^2 (1.0 lb/ft^2) which was considered acceptable. Test results in Table I show that the composite article of Example 4 met all FAA requirements.

Example 5

[0077] A five-ply composite article was prepared having a symmetrical ply construction identical to that in Example 4 except for the central, 3rd ply. In this example, the central ply consisted of 50 layers of high strength polyethylene fibers, unidirectionally aligned within a layer and arranged with the fibers in adjacent layers oriented at 90° to one another. The polyethylene fibers were of 1100 denier, had a tensile strength of about 3.1 Gpa, an initial tensile modulus of about 107 GPa, an elongation-to-break of about 3.3% set forth other yarn physicals and were in a matrix comprising an epoxy vinyl ester resin having a tensile modulus of about 3.5 GPa (500 kpsi) (SPECTRA SHIELD® VE PLUS from Honeywell

International Inc.).

[0078] The plies of the composite article were assembled and bonded together in a press under a pressure of 690 kPa (100 psi) at a temperature of 121°C. for 30 minutes.

[0079] The composite article of Example 5 also had an areal density of 4.89 kg/m^2 (1.0 lb/ft^2), which was considered acceptable. Test results in Table I show that the composite article of Example 5 met all FAA requirements.

[0080] Having thus described the invention in rather full detail, it will be understood that such detail need not be strictly adhered to but that further changes and modifications may suggest themselves to one skilled in the art, all falling within the scope of the invention as defined by the subjoined claims.

TABLE 1

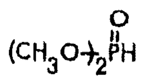
									Vertical Burn Test				
Ex. or Comp. Ex. No	Composite Skin	Intumescent Resinous Composition	Glass Bubbles % of Resin	SPECTRA SHIELD® Ballistic Panel Type	Flexural Modulus, MPa (psi)	Flexural Strength at Yield, MPa (psi)	Heat Release Rating, kW/M^2	Smoke Density, DS (max)	Burning Time sec	Max. Burn Length, cm (inches)	Max. Longest burning particle, sec	Areal Density, Pa (psf)	Vo, m/s (Ft/sec)
FAA Requirements							**<65**	**<200**	**<15**	**<15.2 (<6)**	**<5**		**>436 (>1430)**
Comp. 1	SS	phenolic	30	VE Plus	n.a	n.a	11	95	0	3.81 (1.5)	0	88.1 (1.84)	n.a
Comp. 2	SS	epoxy	0	VE Plus	n.a	n.a	47	n.a	n.a	n.a	n.a	74.7 (1.56)	n.a
1	Al	epoxy	4.7	VE Plus	n.a	n.a	0	n.a	n.a	n.a	n.a	58.4 (1.22)	>436 (>1430)
2	Al	epoxy	4.7	VE Plus	4660 (676,000)	23.1 (3344)	0	16	0	0.51 (0.2)	0	57.0 (1.19)	>436 (>1430)
3	Al	Phenolic	12.9	PCR Plus	606 (87,930)	6.46 (937)	1	9	0	2.03 (0.8)	0	57.0 (1.19)	>436 (>1430)
4	Al	None	0	PCR Plus	n.a	n.a	0	35	0	3.81 (1.5)	0	47.88 (1.00)	>436 (>1430)
5	Al	none	0	VE Plus	n.a	n.a	0	3	0	3.81 (1.5)	0	47.88 (1.00)	>436 (>1430)

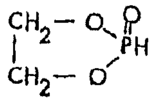
n.a - not available

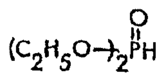
Claims

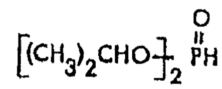
1. A composite article comprised of a plurality of plies bonded together, wherein a first ply is comprised of a metal foil, a second ply is comprised of a fire retardant bonding material, and a third ply is comprised of a plurality of layers, each of said layers comprising a network of flammable polymeric fibers in a matrix, said polymeric fibers having a tenacity of at least 17 g/denier, a tensile modulus of at least 500 g/denier and an energy-to-break of at least 20 Joules/g, wherein the fiber tenacity, tensile modulus and energy-to-break are measured in yarn by ASTM D2256; wherein said fire retardant bonding material comprises intrinsically fire retardant polymers selected from chlorinated polyethylene, polyvinyl chloride, poly(1,1-dichloroethylene), poly(chlorotrifluoroethylene), poly(1,1-dichloro-2-fluoroethylene), poly(1,2-dichloro-1,2-difluoroethylene), poly (1,1-difluoroethylene), poly (1,2-difluroethylene), poly(tetrafluoroethylene), poly(trifluorethylene), poly((pentafluoroethyl) ethylene), poly(tetradecafluoropentylethylene), poly(hexafluoropropylene), poly(2,3,3,3-tetrafluoropropylene), poly(3,3,3-trifluoropropylene), poly(heptafluoropropyl) ethylene), poly(vinylidene fluoride), and poly(tribromostyrol), mixtures thereof, and copolymers of the antecedent monomers comprising these polymers, and melamine-formaldehyde, urea-formaldehyde, phenol-formaldehyde, alternatively, said fire retardant bonding material comprises at least 10% by weight of a polymeric material selected from thermoplastics and thermosets and a fire retardant additive, wherein said fire retardant additive is selected from the following organic additives:

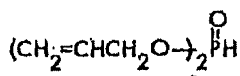
   the following **P-H Functional** compounds

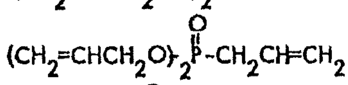


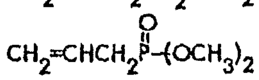


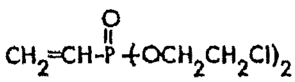


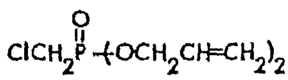


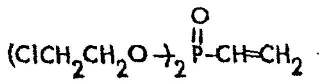


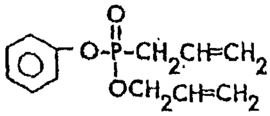












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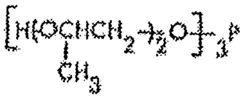

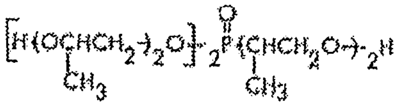

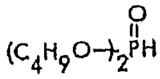

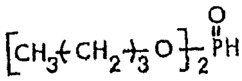

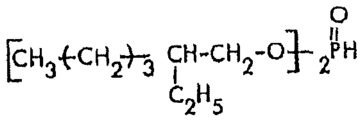

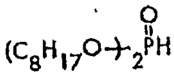

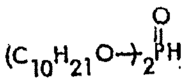

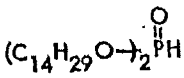

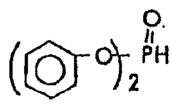

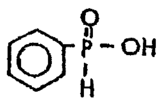

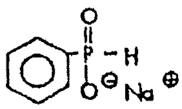

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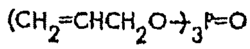

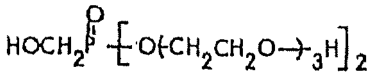

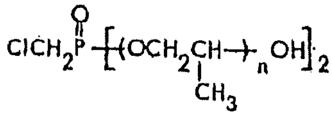

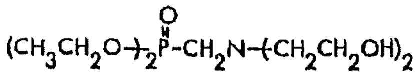

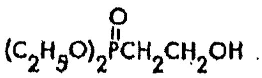

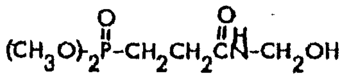

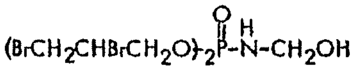

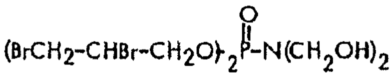

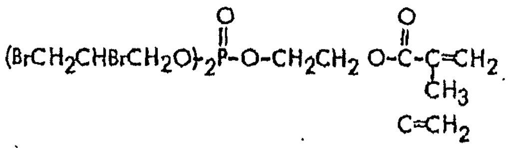

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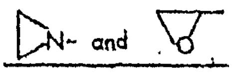
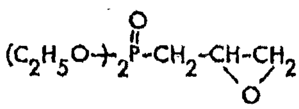
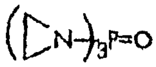
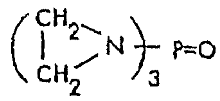


Functional compounds







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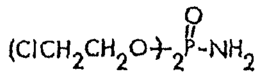

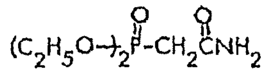

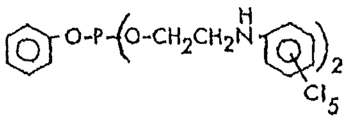

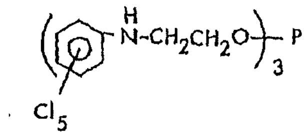

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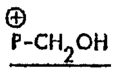
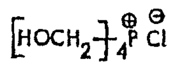
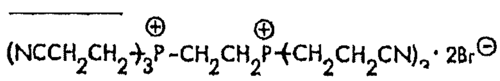


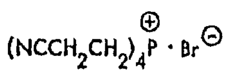
Functional compounds

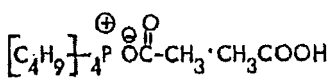


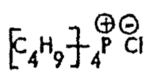
$\oplus \mathbf{P\{CH_2OH)_4A}\ominus$

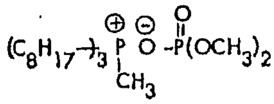
the following $\mathbf{R_4P}\oplus$**Salts** compounds



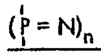




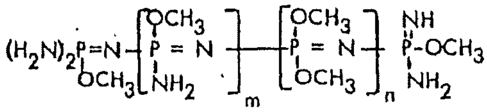


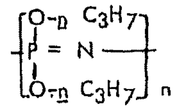


the following



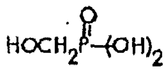
Polymers compounds

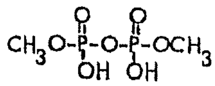


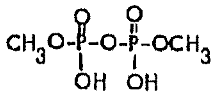


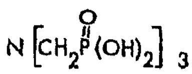
the following

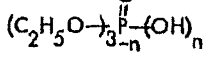
Functional compounds



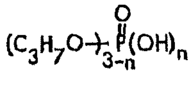








n = 1 to 2



n = 1 to 2

$$BrCH_2CHBrCH_2O\text{-}P(=O)\text{-}(OH)_2$$

(and $NH_4^{\oplus}$ SALT)

$$(BrCH_2CHBrCH_2O)_2P(=O)\text{-}OH$$

(and $NH_4^{\oplus}$ SALT)

$$(C_4H_9O)_{3-n}P(=O)(OH)_n$$

n = 1 to 2

$$(C_4H_9O)_2P(=O)OH$$

$$(C_4H_9O)_{3-n}P(=O)(OH)_n$$

n = 1 to 2

$$(C_4H_9O)_{3-n}P(=O)(OH)_n$$

n = 1 to 2

$$(C_5H_{11}O)_{3-n}P(=O)(OH)_n$$

n = 1 to 2

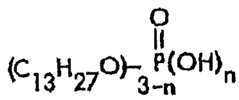
$$(C_8H_{17}O)_2P(=O)OH$$

$$\left[C_8H_{17}O\text{-}P(=O)(OH)\text{-}\right]_2 O$$

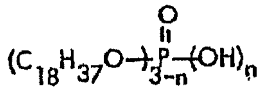
$$(C_8H_{17}O)_{3-n}P(=O)(OH)_n$$

n = 1 to 2

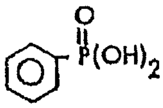
$$(C_{10}H_{21}O)_2P(=O)\text{-}OH$$

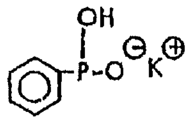


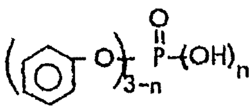
n = 1 to 2



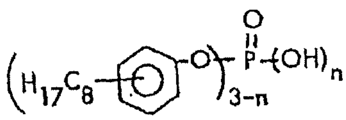
n = 1 to 2





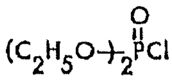


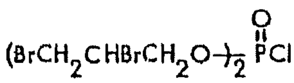
n = 1 to 2

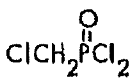


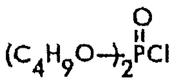
n = 1 to 2

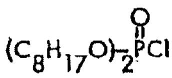
the following **P-Cl Functional** compounds

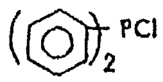


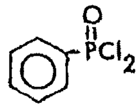








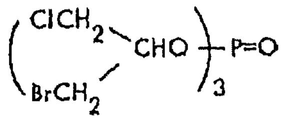




the following **P + S Compounds Functional**

$(CH_3)_2P\text{-}S\text{-}S\text{-}P(CH_3)_2$

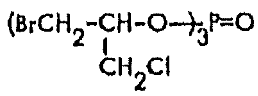
the following **P + Br Compounds**

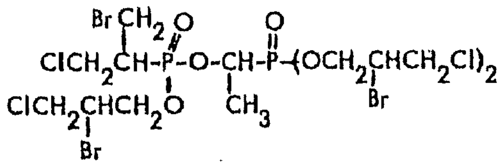


$(BrCH_2CHBrCH_2O\text{-})_3P{=}O$

$(XCH_2CHXCH_2O\text{-})_3P{=}O$

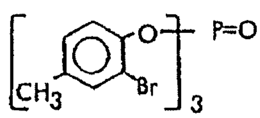
X = Cl, Br

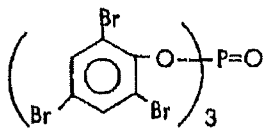




$(BrCH_2CHBrCH_2O)_2P(=O)\text{-}OCH_2CHClCH_2Cl$

$(C_2H_5O\text{-})_2P(=O)\text{-}CH_2CH_2Br$





the following **P + Cl Compounds**

$$(ClCH_2CH_2O)_3P$$

$$[(ClCH_2)_2CHO]_3P{=}O$$

$$(ClCH_2CHClCH_2O)_3P{=}O$$

$$(ClCH_2CH_2CH_2O)_3P{=}O$$

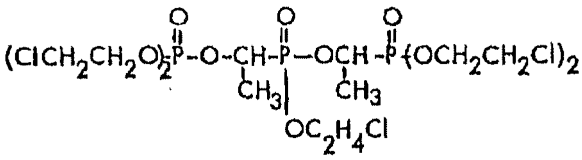
$$(ClCH_2\underset{CH_3}{\underset{|}{C}}H{-}O)_3P{=}O$$

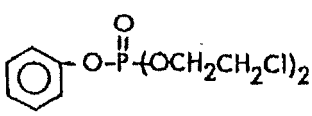
$$(CH_3CHClCH_2O)_3P{=}O$$

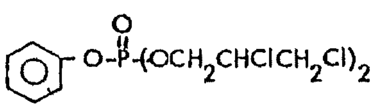
$$C_8H_{17}O{-}\overset{O}{\overset{\|}{P}}(OCH_2CH_2Cl)_2$$

$$ClCH_2CH_2\overset{O}{\overset{\|}{P}}(OCH_2CH_2Cl)_2$$

$$(ClCH_2)_2C[CH_2O\overset{O}{\overset{\|}{P}}(OCH_2CH_2Cl)_2]_2$$







the following **P (Phosphites)**

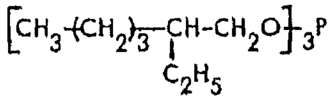
$(CH_3O)_3P$

$(CH_3CH_2O-)_3P$

$[(CH_3)_2CHO]_3P$

$[CH_3-(CH_2)_3O]_3P$

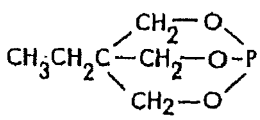
$(C_8H_{17}O-)_3P$

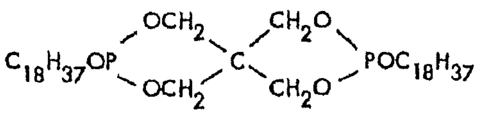


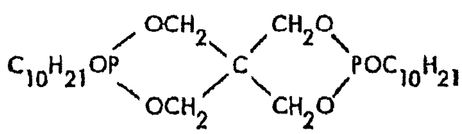
$(C_{12}H_{25}O-)_3P$

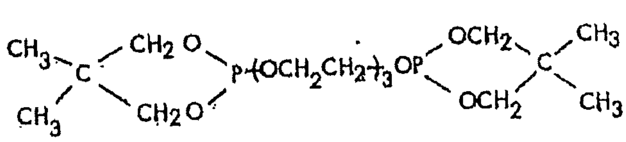
$(C_{18}H_{37}O-)_3P$

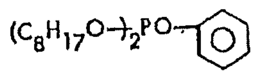
$(C_{18}H_{37}O-)_3P$

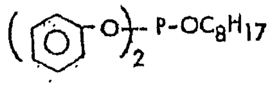


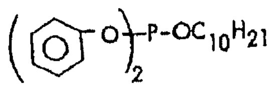


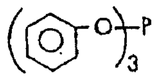


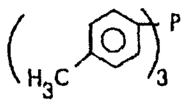


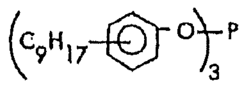












the following **P (Phosphates)**

$$(CH_3O)_3P{=}O$$

$$(C_2H_5O)_3P{=}O$$

$$(C_2H_5O)_3P{=}O$$

$$(C_4H_9O)_3P{=}O$$

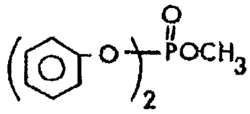
$$(C_8H_{17}O)_3P{=}O$$

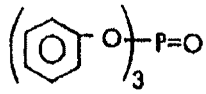
$$(CH_3(CH_2)_3\underset{\displaystyle C_2H_5}{\underset{|}{C}}H{-}CH_3O)_3P{=}O$$

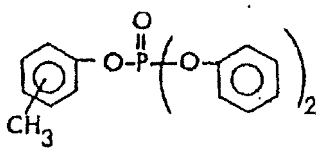
$$(C_8H_{17}O)_3P{=}O$$

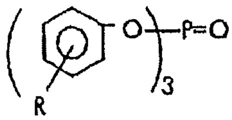
$$(CH_3(CH_2)_3\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}HCH_2O)_3P{=}O$$

$$(C_4H_9O{-}CH_2CH_2O)_3P{=}O$$

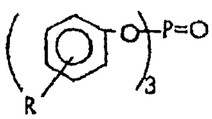




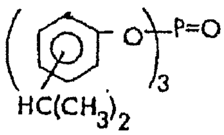


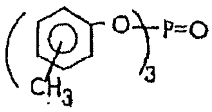


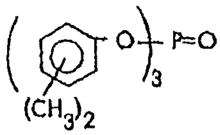
R = H, CH_3

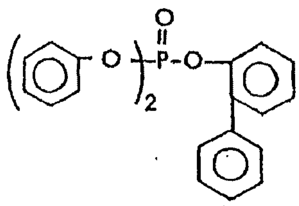


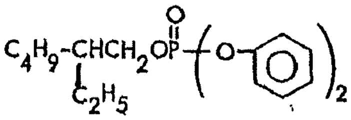
R=H, $(CH_3)_2CH$

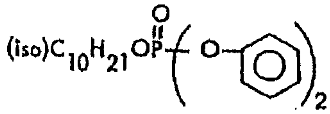




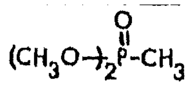


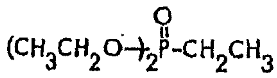


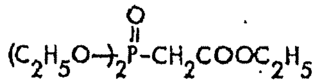


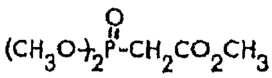


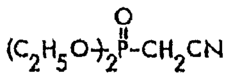
the following **P (Phosphonates)**

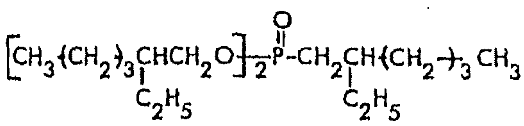


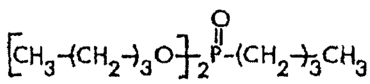


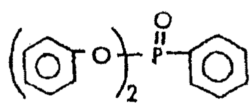




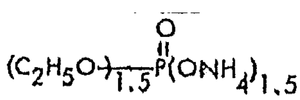


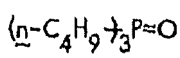


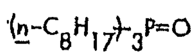


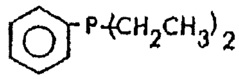


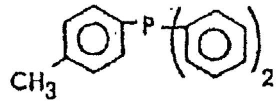
the following **P (Miscellaneous)**

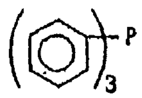


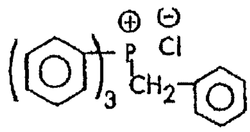


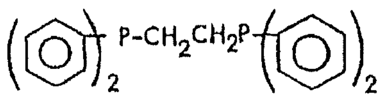


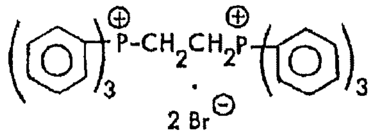


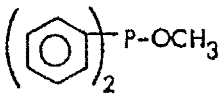


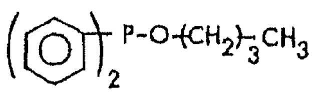


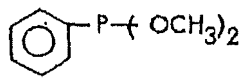


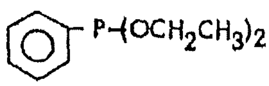


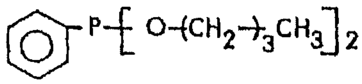


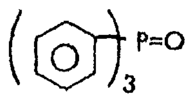












the following **P + S Compounds**

$(C_{12}H_{25}S)_3P$

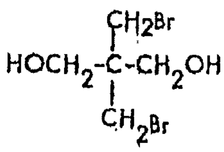
$(CH_3CH_2O)_3P=S$

$[CH_3(CH_2)_3O]_3P=S$

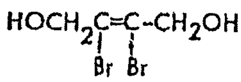
$(C_8H_{17}O)_3P=S$

the following **Bromo - Compounds : -OH Functional** compounds

$(BrCH_2)_3C-OH$

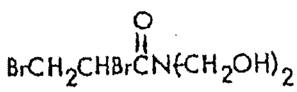


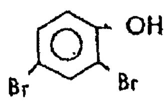
$BrCH=CBr-CH_2OH$

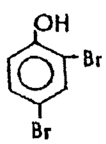


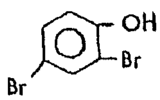
$BrCH_2CH_2OH$

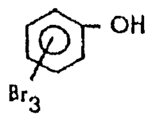
$BrCH_2CHBrCH_2OH$

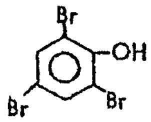


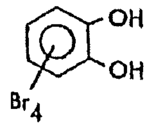


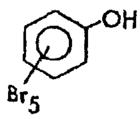


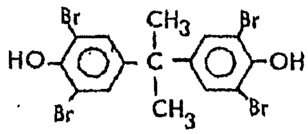


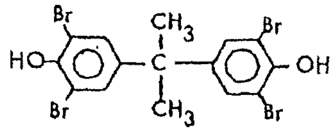


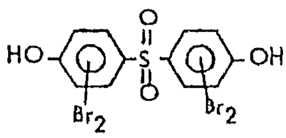


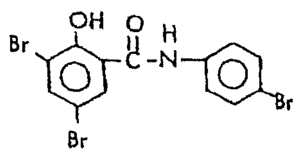


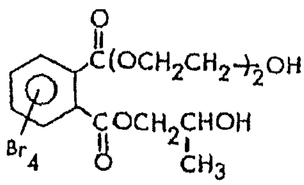


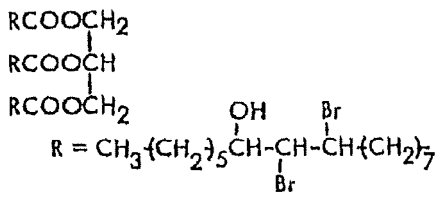


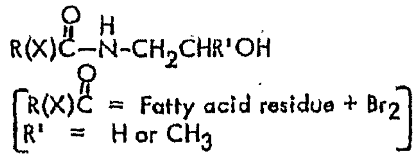


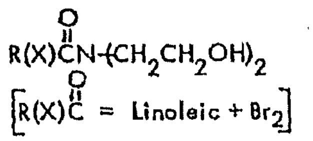


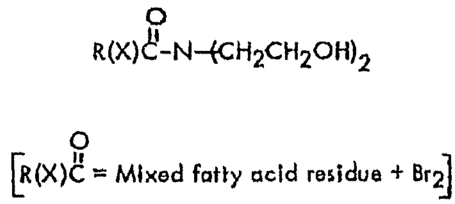




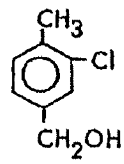


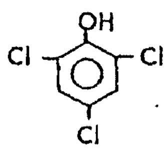


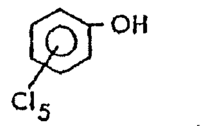


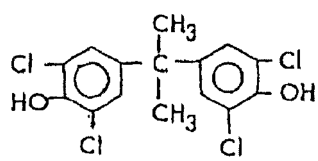


the following <u>**Chloro- Compounds: -OH Functional**</u> compounds

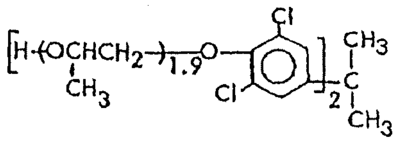


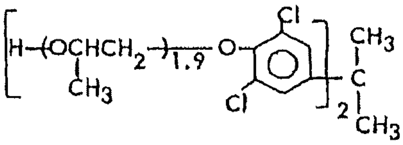


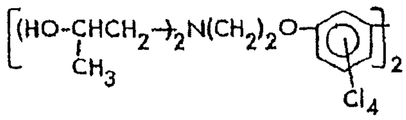


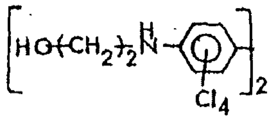


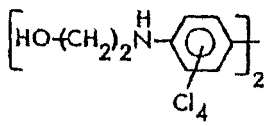
Product of Cl_2 and

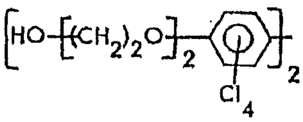




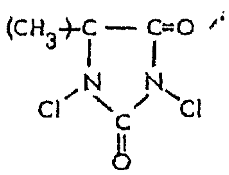


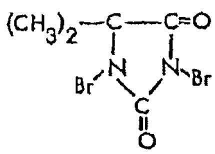


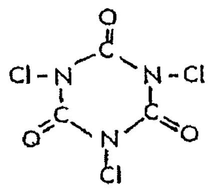




the following **-C≡C- Functional** compounds **$Cl-CH_2-C{\equiv}C-CH_2Cl$**
the following **N-Halogen Functional** compounds

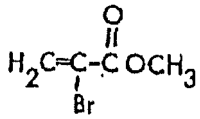


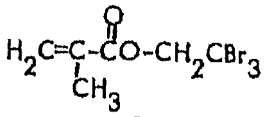


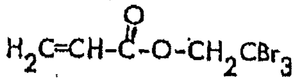


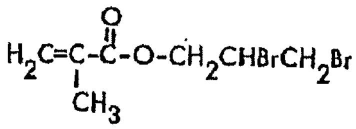
the following **$H_2C{=}C$ - Functional** compounds **$CH_2{=}CH-Br$**

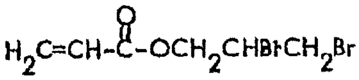
$CH_2=CH-CH_2Br$

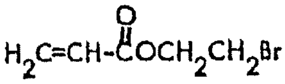


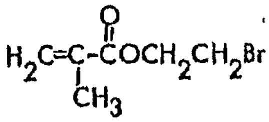


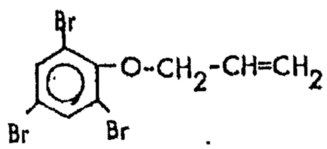


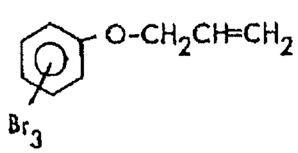


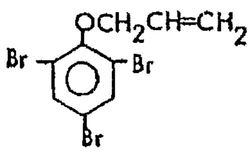


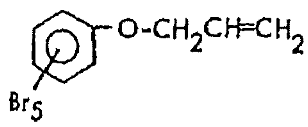


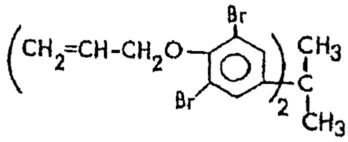


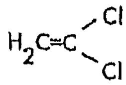




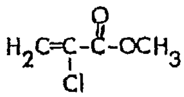


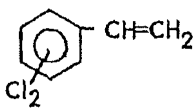


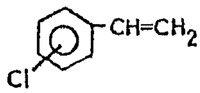


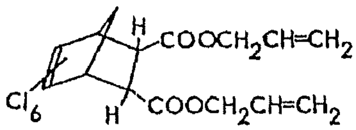


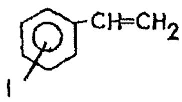
CH_2=CCl_2 CH_2=CH-CH_2Cl





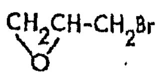


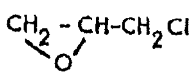


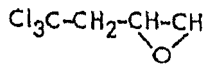


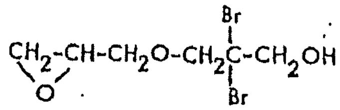
the following

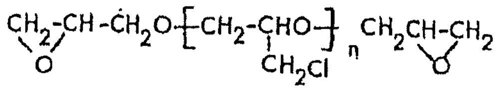
Functional compounds











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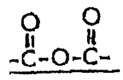
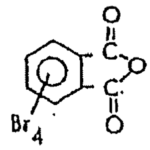
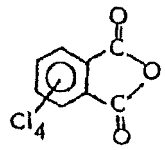
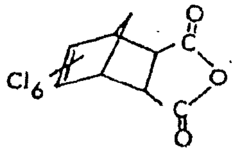
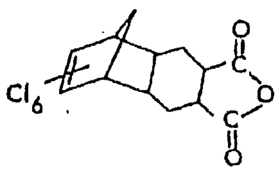


Functional compounds

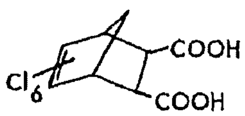


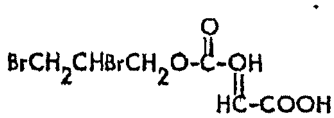






the following **-COOH Functional** compounds



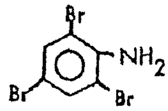


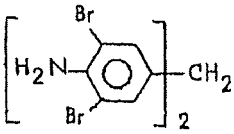
(And NH_4^+ Salt)

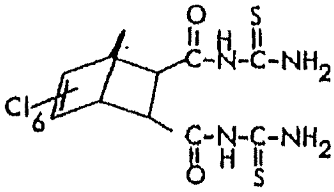
the following **-CHO Functional** compounds **$BrCH_2CHBr$-CHO**

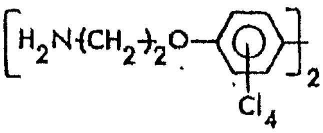
Cl_3C-CHO

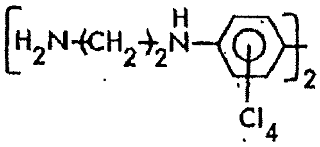
the following **$-NH_2$ Functional** compounds

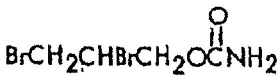












THE FOLLOWING **NON-FUNCTIONAL HALOGEN COMPOUNDS Bromo -Compounds**

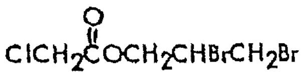
$BrCH_2Cl$

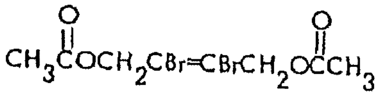
Br_2CH-$CHBr_2$

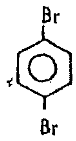
$BrCH_2CH_2CHCl$

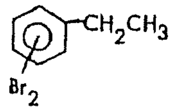
$BrCH_2CHBrCHBrCH_2Br$

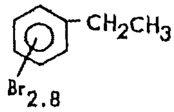
$(BrCH_2CHBrCH_2O)_2CH_2$

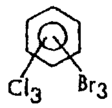


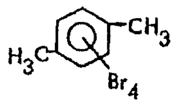


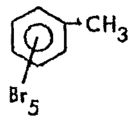


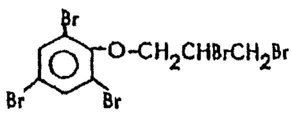


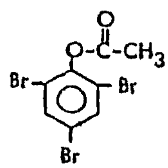


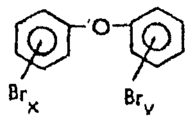




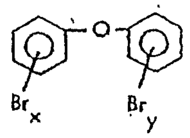




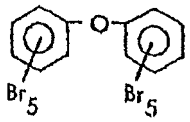


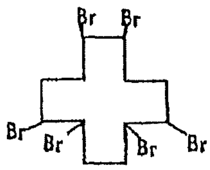


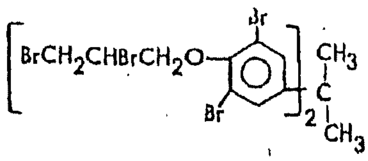
x + y = 5

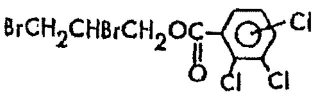


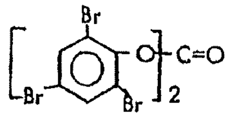
x + y = 8

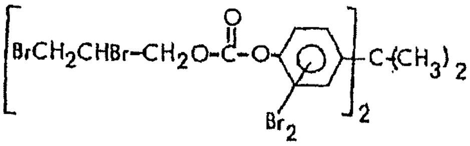


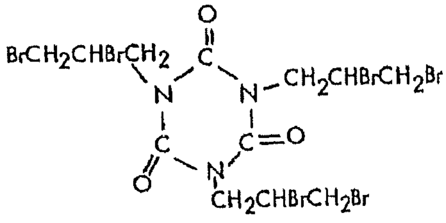


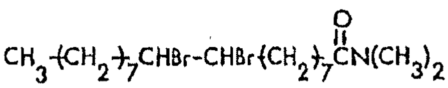










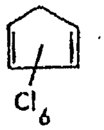


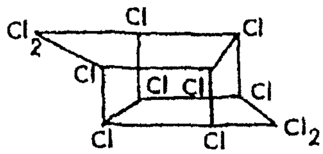
Chloro-Compounds

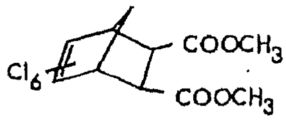
Cl_3C-CCl_3

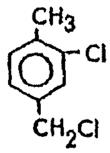
$ClCH_2CHClCH_2Cl$

$Cl_2C=CCl-CCl=CCl_2$



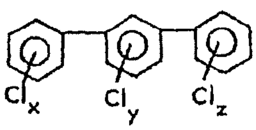


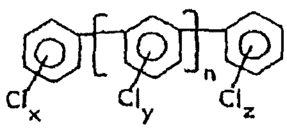




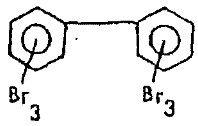
$C_{17}H_{30}Cl_5\overset{O}{\overset{\|}{C}}-OCH_3$

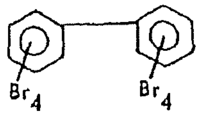
Chloro-Tri (and higher) Phenyls

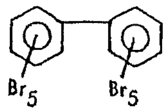


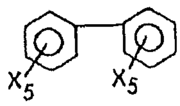


Bromo- and Chloro-Biphenyls

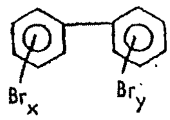




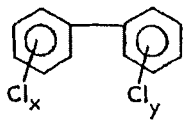




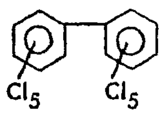
X_6 = Cl
X_4 = Br



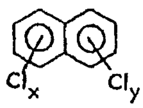
x + y = 8

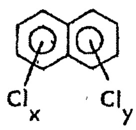


(x + y = 1 - 10)



Chloro- Naphthalenes





HALOGENATED PARAFFINES

$$CY_3\text{-}(CY_2)_n\text{-}CY_3$$

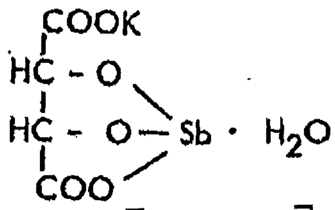
Y = Br, H

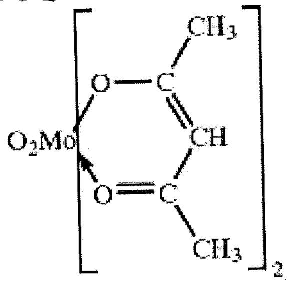
$$CY_3\text{-}(CY_2)_n\text{-}CY_3$$

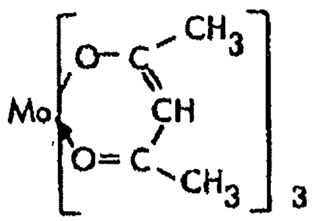
Y = H, Cl

$$Y\text{-}(CY_2\underset{\displaystyle CY_3}{\underset{|}{C}}Y)_n\text{-}Y$$

Y = H, Cl or the following inorganic additives: antimony oxide, antimony sulfides, antimony halides, sodium or potassium antimonite, ammonium, sodium or potassium phosphates, phosphorus halides, phosphonitrilic chloride, phosphorus pentasulfide, sodium borates, sodium, potassium or ammonium tetrafluoroborate, calcium or barium borates, lithium, sodium or potassium tetraborate, boric acid, trimethoxyborozine, aluminum oxide hydrates, aluminophosphate hydrates, sodium silicates, ammonium bromide, ammonium sulfate, lithium silicates, molylbdenum oxide, ammonium paramolybdate, molybdenum sulfide, and sulfamide;
or the following organometallic additives:







and
wherein said network of flammable polymeric fibers include flammable fibers selected from unmodified poly-

olefins, polyesters, polyvinyl alcohol and polyacrylamide.

2. The composite article of Claim 1, additionally comprised of a fourth ply comprising a fire retardant bonding material as defined in claim 1, and a fifth ply comprising a metal foil.

3. The composite article of Claim 1, additionally comprising an intumescent resinous composition ply between said first and said second plies,
wherein said intumescent resinous composition comprises a spumific selected from the group consisting of melamine, melamine salts, melamine derivatives, urea, dicyandiamide and guanidine dispersed in a resin selected from the group consisting of phenolic polymers, melamine polymers, epoxies, silicones, unsaturated polyesters, and thermosetting polyurethanes.

4. The composite article of Claim 3, additionally comprising a fifth ply consisting of an intumescent resinous composition, a sixth ply comprised of a fire retardant bonding material as defined in claim 1, and a seventh ply comprised of a metal foil,
wherein said intumescent resinous composition comprises a spumific selected from the group consisting of melamine, melamine salts, melamine derivatives, urea, dicyandiamide and guanidine dispersed in a resin selected from the group consisting of phenolic polymers, melamine polymers, epoxies, silicones, unsaturated polyesters, and thermosetting polyurethanes.

5. The composite article of Claim 1 or Claim 3, wherein said metal foil is aluminum having a thickness from 0.0005 inches (12.7 micrometers) to 0.005 inches (127 micrometers).

6. The composite article of Claim 1 or Claim 3, wherein said fire retardant bonding material is a blend of antimony oxide (Sb_2O_3), decabromodiphenyl ether and polychlorinated paraffin wax in a polyacrylate resin binder.

7. The composite article of Claim 1 or Claim 3, wherein said flammable polymeric fibers are polyethylene.

8. The composite article of Claim 7, wherein said polyethylene fibers are unidirectionally oriented within a layer, and wherein fibers in adjacent layers are oriented at 90° to one another.

9. The composite article of Claims 3 or 4, wherein said intumescent resinous composition further comprises a carbonific that is an organic polyhydroxy compound.

10. The composite article of Claim 10, wherein said organic polyhydroxy compound is selected from pentaerythritol, dipentaerythritol, tripentaerythritol, starch or a sugar.

11. The composite article of any one of claims 3, 4, 9 and 10, wherein said intumescent resinous composition further comprises an acid forming substance that is selected from aminophosphate, ammonium phosphates, amine phosphates, ammonium polyphosphates, and melamine phosphate.

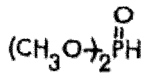
12. The composite article of any one of Claims 1-5 or 7-11, wherein said fire retardant material comprises an intrinsically fire retardant polymer as defined in claim 1.

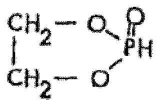
Patentansprüche

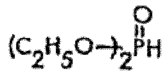
1. Verbundgegenstand, der aus mehreren miteinander verbundenen Lagen besteht, wobei eine erste Lage aus einer Metallfolie besteht,
eine zweite Lage aus einem feuerhemmenden Verbindungsmaterial besteht, und
eine dritte Lage aus mehreren Schichten besteht, wobei jede dieser Schichten ein Netzwerk von entflammbaren Polymerfasern in einer Matrix umfasst, wobei die Polymerfasern eine Festigkeit von mindestens 17 g/Denier, ein Zugmodul von mindestens 500 g/Denier und eine Bruchenergie von mindestens 20 Joule/g aufweisen,
wobei Faserfestigkeit, Zugmodul und Bruchenergie des Garns nach ASTM D2256 gemessen werden;
wobei das feuerhemmende Verbindungsmaterial spezifisch feuerhemmende Polymere umfasst, ausgewählt aus chloriertem Polyethylen, Polyvinylchlorid, Poly(1,1-dichlorethylen), Poly(chlortrifluorethylen), Poly(1,1-dichlor-2-fluorethylen), Poly(1,2-dichlor-1,2-difluorethylen), Poly(1,1-difluorethylen), Poly(1,2-difluorethylen), Poly(tetrafluorethylen), Poly(trifluorethylen), Poly((pentafluorethyl)ethylen), Poly(tetradecafluorpentylethylen), Poly(hexafluorpro-

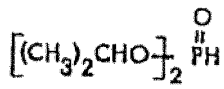
pylen), Poly(2,3,3,3-tetrafluorpropylen), Poly(3,3,3-trifluorpropylen), Poly(heptafluorpropyl)ethylen), Poly(vinylidenfluorid) und Poly(tribromstyrol), Mischungen davon und Copolymere der Vorläufermonomere, umfassend diese Polymere und Melaminformaldehyd, Harnstoffformaldehyd Phenolformaldehyd,
wobei das feuerhemmende Verbindungsmaterial alternativ mindestens 10 Gew.-% eines Polymermaterials umfasst, ausgewählt aus Thermoplasten und Duroplasten und einem feuerhemmenden Zusatzstoff, wobei der feuerhemmende Zusatzstoff ausgewählt ist aus den folgenden organischen Zusatzstoffen:

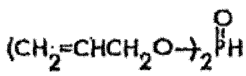
den folgenden **P-H-funktionellen** Verbindungen

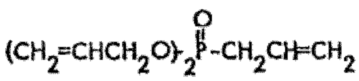


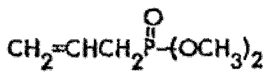


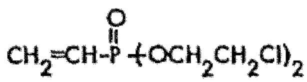


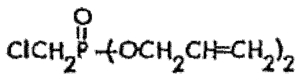


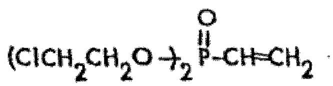


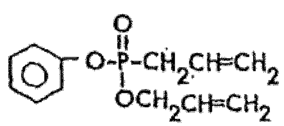




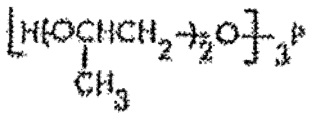


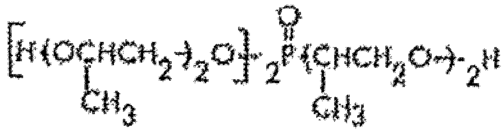






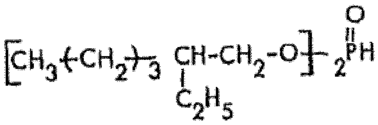
den folgenden **-OH-funktionellen** Verbindungen





$$(C_4H_9O)_2\overset{O}{\overset{\|}{P}}H$$

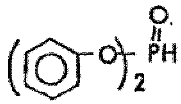
$$[CH_3(CH_2)_3O]_2\overset{O}{\overset{\|}{P}}H$$

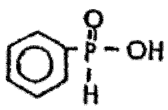


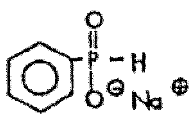
$$(C_8H_{17}O)_2\overset{O}{\overset{\|}{P}}H$$

$$(C_{10}H_{21}O)_2\overset{O}{\overset{\|}{P}}H$$

$$(C_{14}H_{29}O)_2\overset{O}{\overset{\|}{P}}H$$

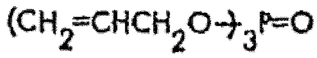


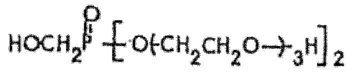


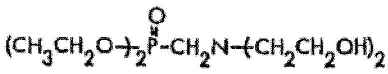


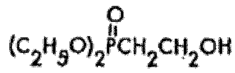
den folgenden **CH_2=CH--funktionellen** Verbindungen

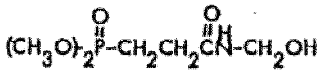
$$(CH_2{=}CHCH_2O)_3P$$

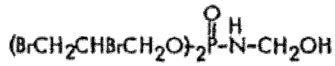


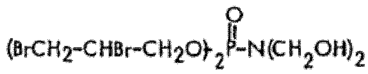


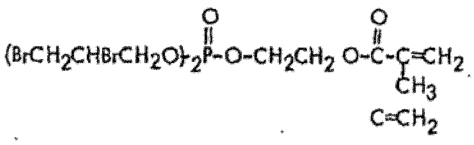




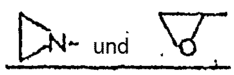




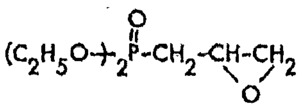


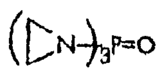


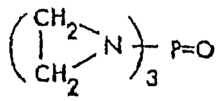
den folgenden



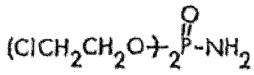
funktionellen Verbindungen

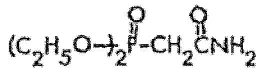


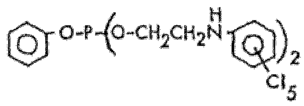


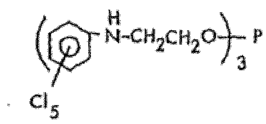


den folgenden **-NH-funktionellen** Verbindungen

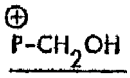




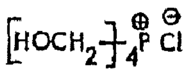


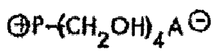


den folgenden

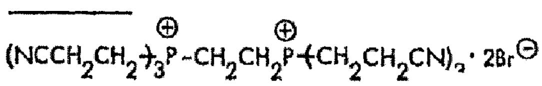


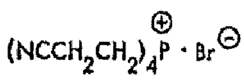
funktionellen Verbindungen

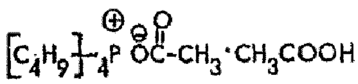


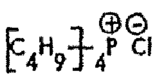


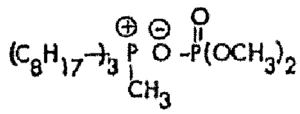
den folgenden **$R_4P\oplus$ Salz**verbindungen



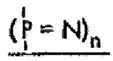




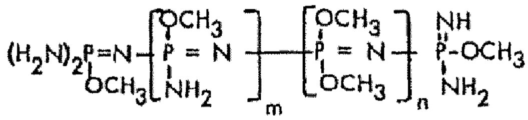


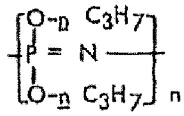


den folgenden

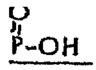


Polymerverbindungen

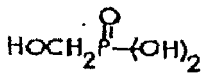


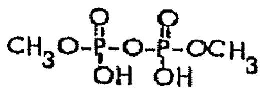


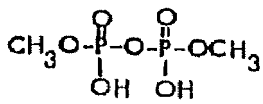
den folgenden

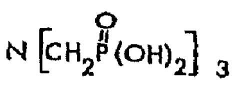


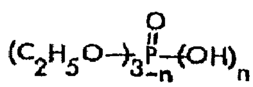
funktionellen Verbindungen



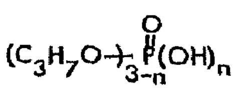








n = 1 bis 2



n = 1 bis 2

$$BrCH_2CHBrCH_2O-\overset{O}{\overset{\|}{P}}-(OH)_2$$

(und $NH_4^{\oplus}$ SALZ)

$$(BrCH_2CHBrCH_2O)_2-\overset{O}{\overset{\|}{P}}-OH$$

(und $NH_4^{\oplus}$ SALZ)

$$(C_4H_9O)_{3-n}\overset{O}{\overset{\|}{P}}(OH)_n$$

n = 1 bis 2

$$(C_4H_9O)_2\overset{O}{\overset{\|}{P}}OH$$

$$(C_4H_9O)_{3-n}\overset{O}{\overset{\|}{P}}-(OH)_n$$

n = 1 bis 2

$$(C_4H_9O)_{3-n}\overset{O}{\overset{\|}{P}}-(OH)_n$$

n = 1 bis 2

$$(C_5H_{11}O)_{3-n}\overset{O}{\overset{\|}{P}}-(OH)_n$$

n = 1 bis 2

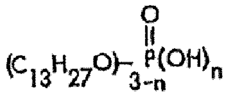
$$(C_8H_{17}O)_2\overset{O}{\overset{\|}{P}}OH$$

$$\left[C_8H_{17}O-\underset{OH}{\overset{O}{\overset{\|}{P}}}-\right]_2 O$$

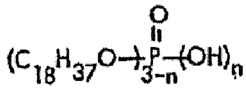
$$(C_8H_{17}O)_{3-n}\overset{O}{\overset{\|}{P}}(OH)_n$$

n = 1 bis 2

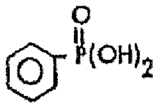
$$(C_{10}H_{21}O)_2\overset{O}{\overset{\|}{P}}-OH$$

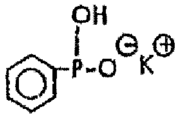


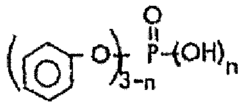
n = 1 bis 2



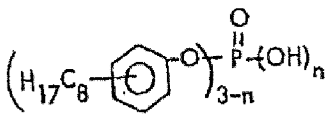
n = 1 bis 2







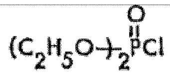
n = 1 bis 2

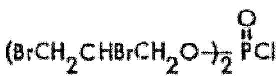


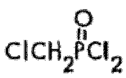
n = 1 bis 2

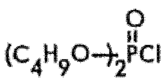
den folgenden **P-Cl-funktionellen** Verbindungen

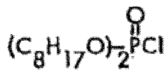
den folgenden **P-Cl-funktionellen** Verbindungen







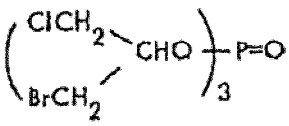


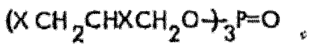


den folgenden **funktionellen P- und S-Verbindungen**

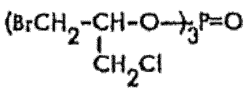
$(CH_3)_2P\text{-}S\text{-}S\text{-}P(CH_3)_2$

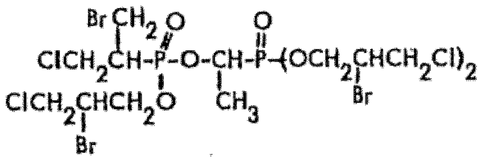
den folgenden **P- und Br-Verbindungen**

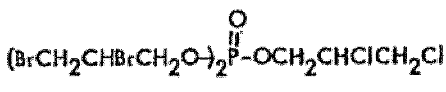


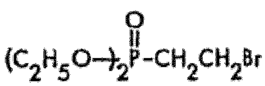


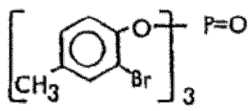
X = Cl, Br

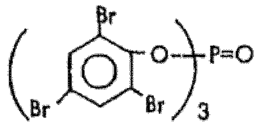












den folgenden **P- und Cl-Verbindungen**

$$(ClCH_2CH_2O-)_3P$$

$$[(ClCH_2)_2CHO]_3P{=}O$$

$$(ClCH_2CHClCH_2O-)_3P{=}O$$

$$(ClCH_2CH_2CH_2O-)_3P{=}O$$

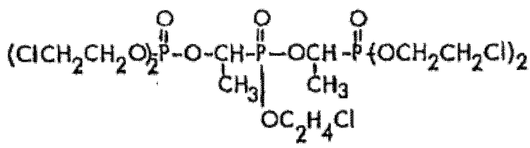
$$(ClCH_2\underset{CH_3}{\underset{|}{C}}H-O-)_3P{=}O$$

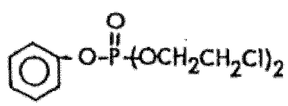
$$(CH_3CHClCH_2O-)_3P{=}O$$

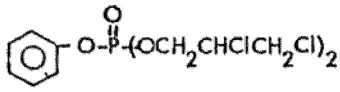
$$C_8H_{17}O-\overset{O}{\overset{\parallel}{P}}-(OCH_2CH_2Cl)_2$$

$$ClCH_2CH_2\overset{O}{\overset{\parallel}{P}}-(OCH_2CH_2Cl)_2$$

$$(ClCH_2)_2C-\left[CH_2O\overset{O}{\overset{\parallel}{P}}(OCH_2CH_2Cl)_2\right]_2$$







den folgenden **P (Phosphiten)**

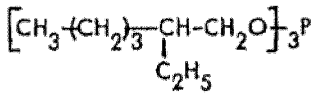
$$(CH_3O)_3P$$

$$(CH_3CH_2O)_3P$$

$$[(CH_3)_2CHO]_3P$$

$$[CH_3(CH_2)_3O]_3P$$

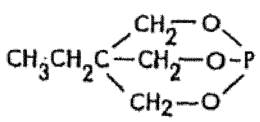
$$(C_8H_{17}O)_3P$$

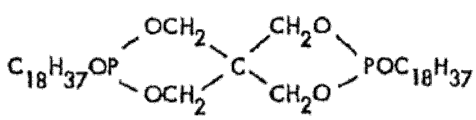


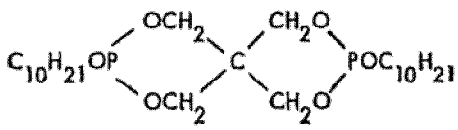
$$(C_{12}H_{25}O)_3P$$

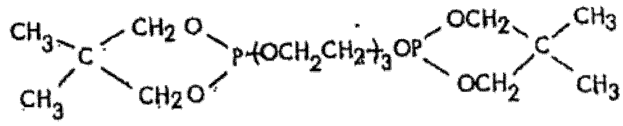
$$(C_{18}H_{37}O)_3P$$

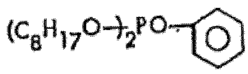
$$(C_{18}H_{37}O)_3P$$

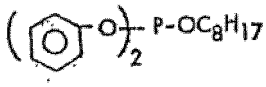


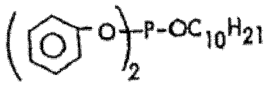


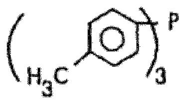












den folgenden **<u>P (Phosphaten)</u>**

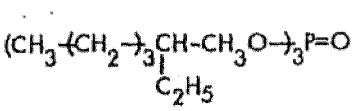
$$(CH_3O-)_3P=O$$

$$(C_2H_5O)_3P=O$$

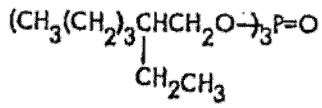
$$(C_2H_5O-)_3P=O$$

$$(C_4H_9O-)_3P=O$$

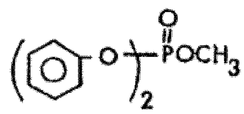
$$(C_8H_{17}O-)_3P=O$$

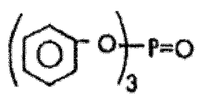


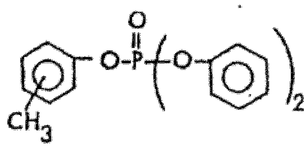
$$(C_8H_{17}O-)_3P=O$$

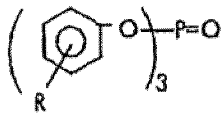


$$(C_4H_9O-CH_2CH_2O-)_3P=O$$



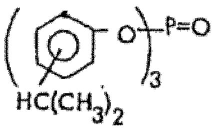


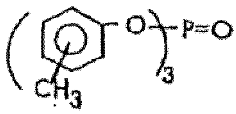


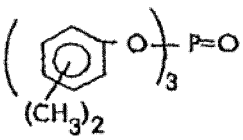


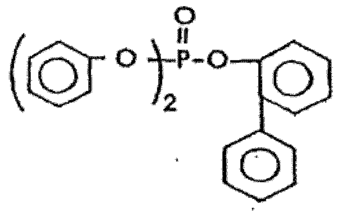
R = H, CH_3

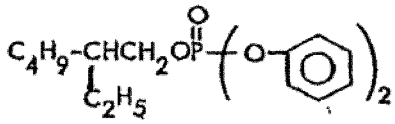
R=H, $(CH_3)_2CH$

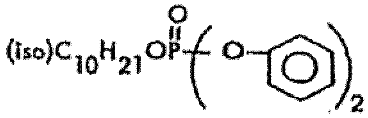




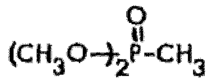


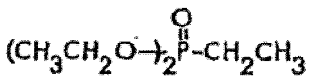


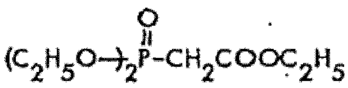


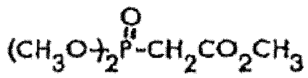


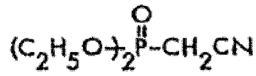
den folgenden **P (Phosphonaten)**

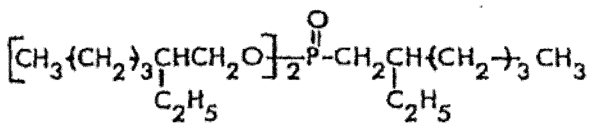


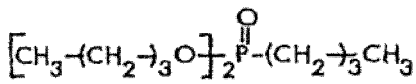


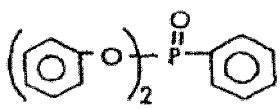










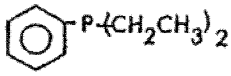


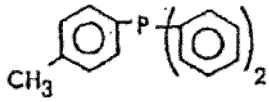
den folgenden **P (Verschiedene)**

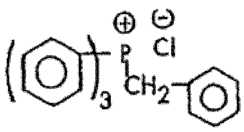
$$(C_2H_5O)_{1.5}\overset{O}{\overset{\|}{P}}(ONH_4)_{1.5}$$

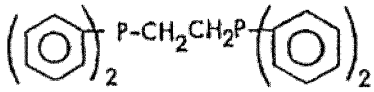
$$(n\text{-}C_4H_9)_3P{=}O$$

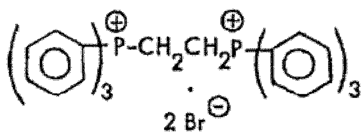
$$(n\text{-}C_8H_{17})_3P{=}O$$

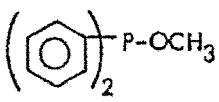


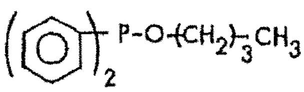


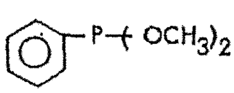


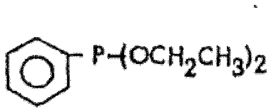


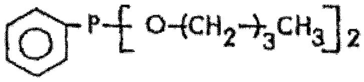












den folgenden **P- und S-Verbindungen**

$(C_{12}H_{25}S)_3P$

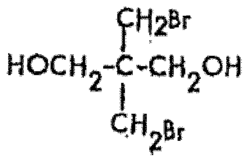
$(CH_3CH_2O)_3P{=}S$

$[CH_3(CH_2)_3O]_3P{=}S$

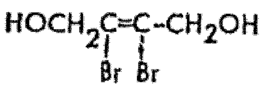
$(C_8H_{17}O)_3P{=}S$

den folgenden **Brom-Verbindungen: -OH-funktionellen** Verbindungen

$(BrCH_2)_3C{-}OH$

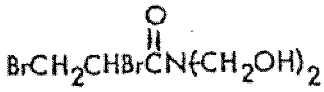


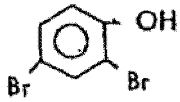
$BrCH{=}CBr{-}CH_2OH$

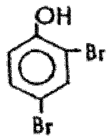


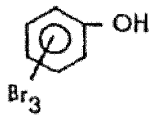
$BrCH_2CH_2OH$

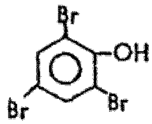
$BrCH_2CHBrCH_2OH$

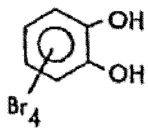


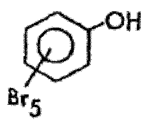


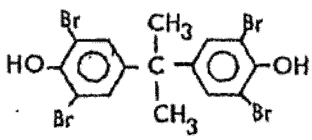


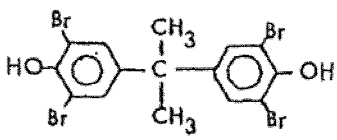


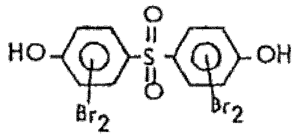


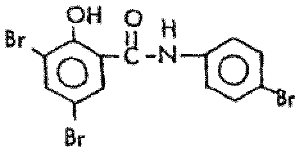


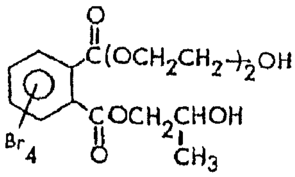


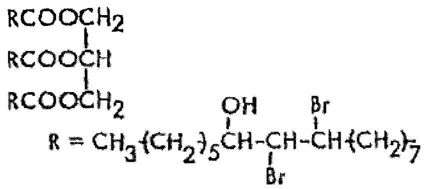


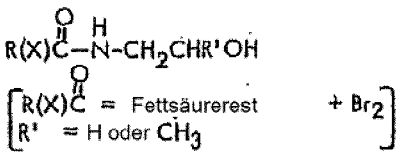


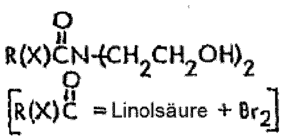


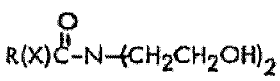




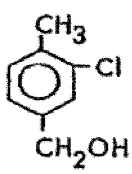


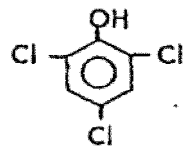


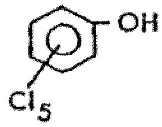


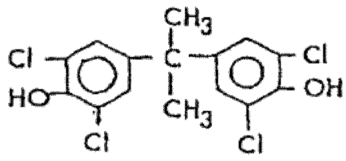


den folgenden **Chlor-Verbindungen: -OH-funktionellen** Verbindungen

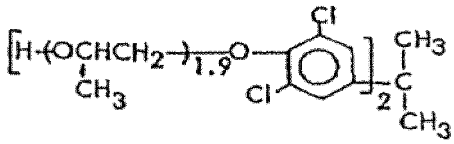


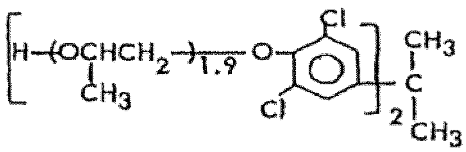


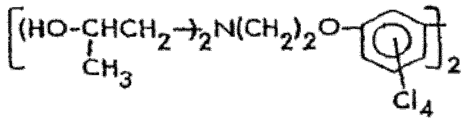


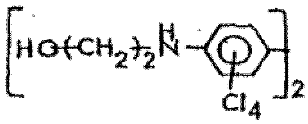


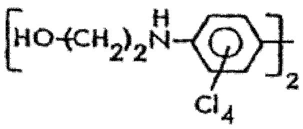
dem Produkt von Cl_2 und

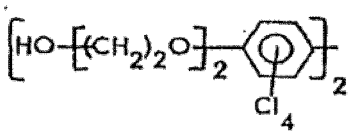




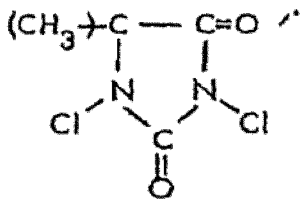


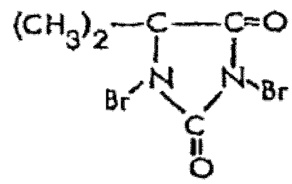


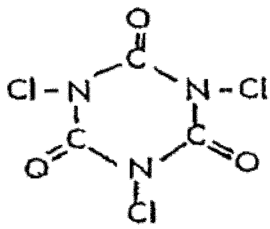




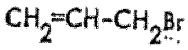
den folgenden **-C≡C- -funktionellen** Verbindungen $Cl\text{-}CH_2\text{-}C{\equiv}C\text{-}CH_2Cl$
den folgenden **N-Halogen-funktionellen** Verbindungen

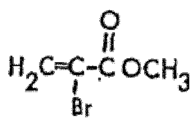


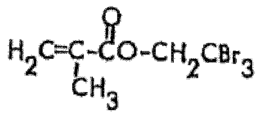


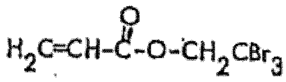


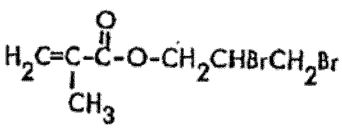
den folgenden **H_2C = C - -funktionellen** Verbindungen **CH_2=CH-Br**

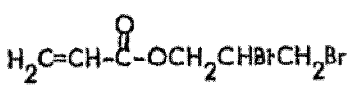


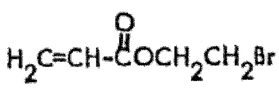


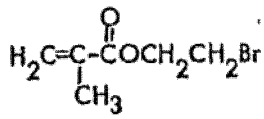


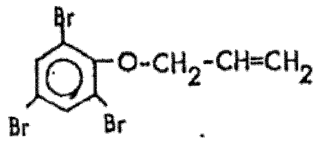


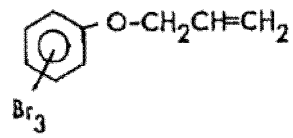


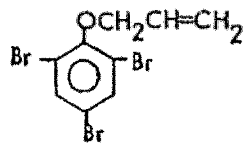


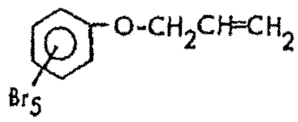


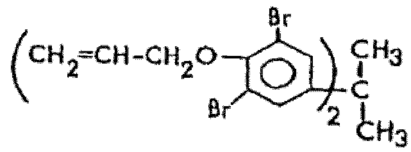


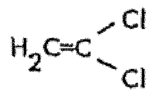






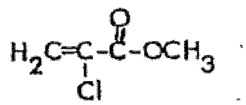


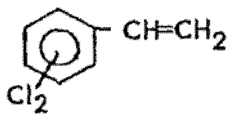


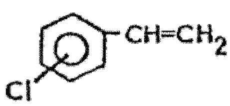


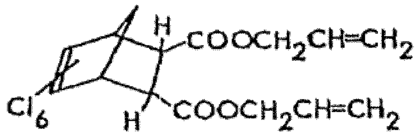
$CH_2{=}CCl_2$

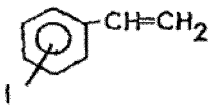
$CH_2{=}CH{-}CH_2Cl$





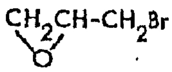


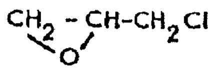


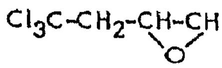


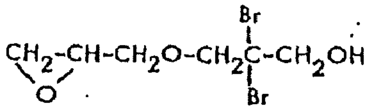
den folgenden

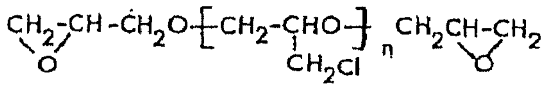
funktionellen Verbindungen



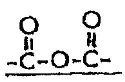




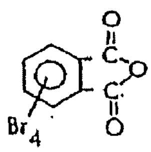


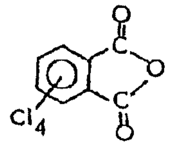


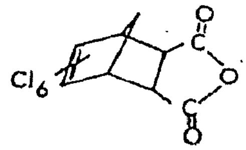
den folgenden

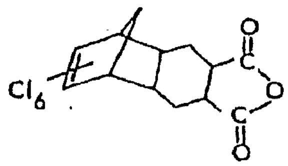


funktionellen Verbindungen

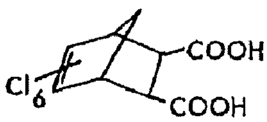


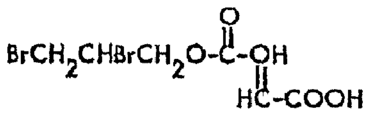






den folgenden **-COOH-funktionellen** Verbindungen

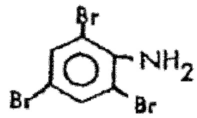


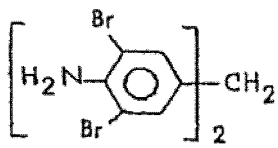


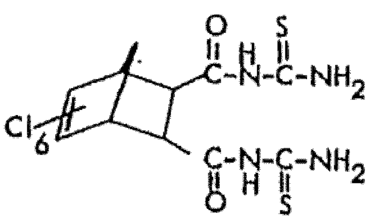
(und NH_4^+ Salz)
den folgenden **-CHO-funktionellen** Verbindungen **$BrCH_2CHBr$-CHO**

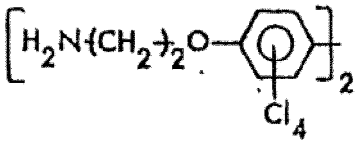
Cl_3C-CHO

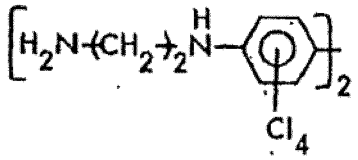
den folgenden **$-NH_2$-funktionellen** Verbindungen

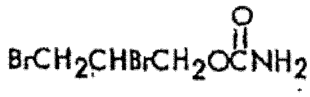












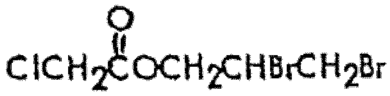
DEN FOLGENDEN **NICHT-FUNKTIONELLEN HALOGEN-VERBINDUNGEN Brom-Verbindungen** **$BrCH_2Cl$**

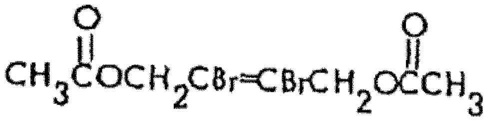
$Br_2CH\text{-}CHBr_2$

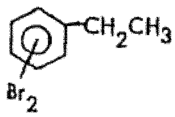
$BrCH_2CH_2CHCl$

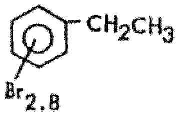
$BrCH_2CHBrCHBrCH_2Br$

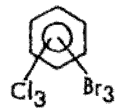
$(BrCH_2CHBrCH_2O)_2CH_2$

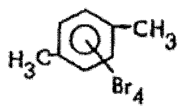


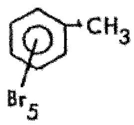


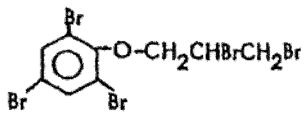


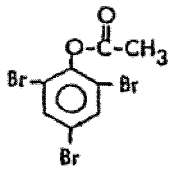


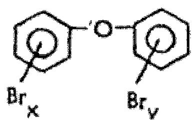




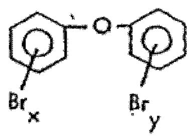




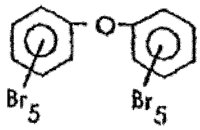


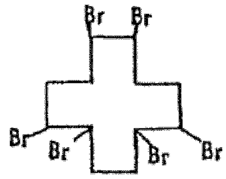


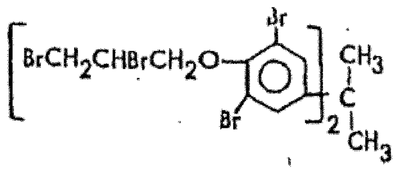
$x + y = 5.$

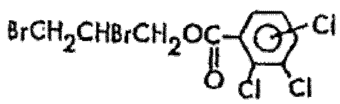


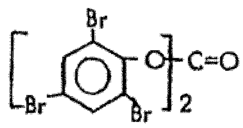
$x + y = 8$

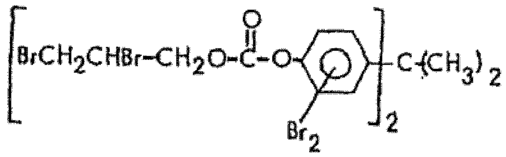


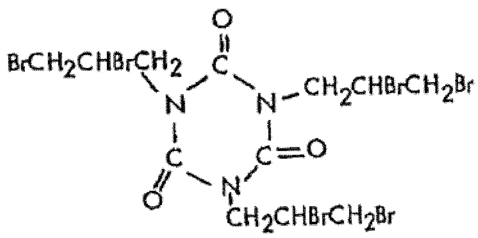


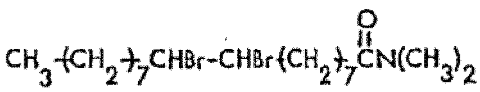










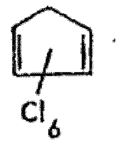


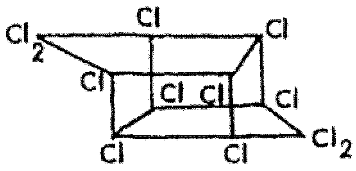
Chlor-Verbindungen

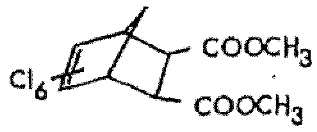
$Cl_3C\text{-}CCl_3$

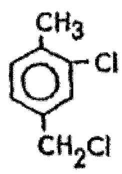
$ClCH_2CHClCH_2Cl$

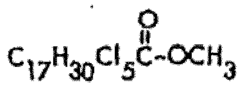
$Cl_2C{=}CCl\text{-}CCl{=}CCl_2$



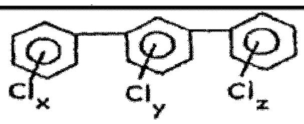




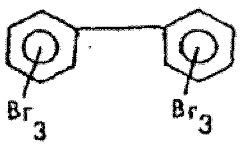


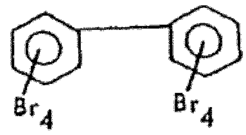


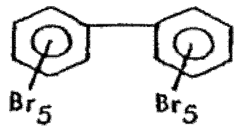
Chlor-Tri- (und höheren) Phenylen



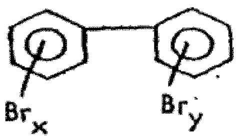
Brom- und Chlor-Bisphenylen



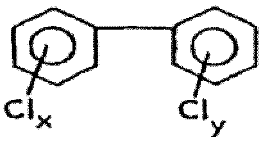




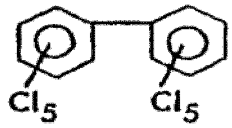
X_6 = Cl
X_4 = Br



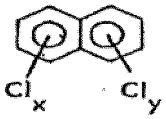
x + y = 8



(x + y = 1 - 10)



Chlor-Naphthalenen



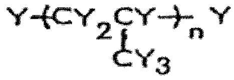
HALOGENIERTEN PARAFFINEN

$$CY_3 \leftarrow\!\!(CY_2\!\!\rightarrow_n CY_3$$

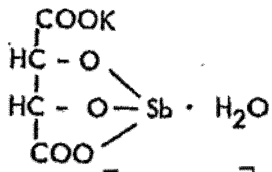
Y = Br, H

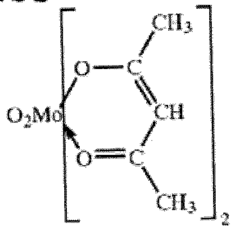
$$CY_3-(CY_2)_n-CY_3$$

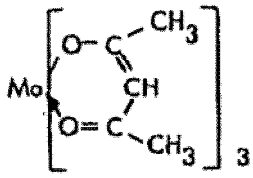
Y = H, Cl

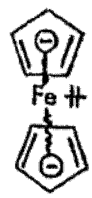


Y = H, Cl oder den folgenden anorganischen Zusatzstoffen: Antimonoxid, Antimonsulfiden, Antimonhaliden, Natrium- oder Kaliumantimonit, Ammonium-, Natrium- oder Kaliumphosphaten, Phosphorhaliden, Phosphonitrilchlorid, Phosphorpentasulfid, Natriumboraten, Natrium-, Kalium- oder Ammoniumtetrafluorborat, Calcium- oder Bariumboraten, Lithium-, Natrium- oder Kaliumtetraborat, Borsäure, Trimethoxyborazin, Aluminiumoxidhydraten, Aluminophosphathydraten, Natriumsilicaten, Ammoniumbromid, Ammoniumsulfat, Lithiumsilicaten, Molylbdänoxid, Ammoniumparamolybdat, Molybdänsulfid, und - sulfamid;
oder den folgenden metallorganischen Zusatzstoffen:









und
wobei das Netzwerk aus entflammbaren Polymerfasern entflammbare Fasern enthält, ausgewählt aus unmodifizierten Polyolefinen, Polyestern, Polyvinylalkohol und Polyacrylamid.

2. Verbundgegenstand nach Anspruch 1, der zusätzlich aus einer vierten Lage, umfassend ein feuerhemmendes Verbindungsmaterial nach Anspruch 1 und einer fünfte Lage, umfassend eine Metallfolie, besteht.

3. Verbundgegenstand nach Anspruch 1, der zwischen der ersten und der zweiten Lage zusätzlich eine intumeszierende Harzzusammensetzungslage umfasst,
wobei die intumeszierende Harzzusammensetzung einen Schaumbildner umfasst, ausgewählt aus der Gruppe

bestehend aus Melamin, Melaminsalzen, Melaminderivaten, Harnstoff, Dicyandiamid und Guanidin, dispergiert in einem Harz, ausgewählt aus der Gruppe bestehend aus Phenolpolymeren, Melaminpolymeren, Epoxiden, Siliconen, ungesättigten Polyestern und duroplastischen Polyurethanen.

4. Verbundgegenstand nach Anspruch 3, der zusätzlich eine fünfte Lage, die aus einer intumeszierenden Harzzusammensetzung besteht, eine sechste Lage, die aus einem feuerhemmenden Verbindungsmaterial nach Anspruch 1 besteht, und eine siebte Lage, die aus einer Metallfolie besteht, umfasst,
wobei die intumeszierende Harzzusammensetzung einen Schaumbildner umfasst, ausgewählt aus der Gruppe bestehend aus Melamin, Melaminsalzen, Melaminderivaten, Harnstoff, Dicyandiamid und Guanidin, dispergiert in einem Harz, ausgewählt aus der Gruppe bestehend aus Phenolpolymeren, Melaminpolymeren, Epoxiden, Siliconen, ungesättigten Polyestern und duroplastischen Polyurethanen.

5. Verbundgegenstand nach Anspruch 1 oder Anspruch 3, wobei die Metallfolie Aluminium mit einer Dicke von 0,0005 Inch (12,7 Mikrometer) bis 0,005 Inch (127 Mikrometer) ist.

6. Verbundgegenstand nach Anspruch 1 oder Anspruch 3, wobei das feuerhemmende Verbindungsmaterial ein Gemisch aus Antimonoxid (Sb_2O_3), Decabromdiphenylether und polychloriertem Paraffinwachs in einem Polyacrylatharzbindemittel ist.

7. Verbundgegenstand nach Anspruch 1 oder Anspruch 3, wobei die entflammbaren Polymerfasern Polyethylen sind.

8. Verbundgegenstand nach Anspruch 7, wobei die Polyethylenfasern innerhalb einer Schicht unidirektional ausgerichtet sind und wobei Fasern in benachbarten Schichten mit 90° zueinander ausgerichtet sind.

9. Verbundgegenstand nach den Ansprüchen 3 oder 4, wobei die intumeszierende Harzzusammensetzung ferner einen Kohlenstoffbildner umfasst, der eine organische Polyhydroxyverbindung ist.

10. Verbundgegenstand nach Anspruch 10, wobei die organische Polyhydroxyverbindung ausgewählt ist aus Pentaerythritol, Dipentaerythritol, Tripentaerythritol, Stärke oder einem Zucker.

11. Verbundgegenstand nach einem der Ansprüche 3, 4, 9 und 10, wobei die intumeszierende Harzzusammensetzung ferner eine säurebildende Substanz umfasst, die ausgewählt ist aus Aminophosphat, Ammoniumphosphaten, Aminphosphaten, Ammoniumpolyphosphaten und Melaminphosphat.

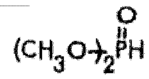
12. Verbundgegenstand nach einem der Ansprüche 1-5 oder 7-11, wobei das feuerhemmende Material ein spezifisch feuerhemmendes Polymer wie in Anspruch 1 definiert umfasst.

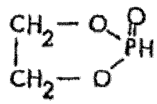
Revendications

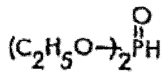
1. Article composite constitué d'une pluralité d'épaisseurs liées les unes aux autres, dans lequel
une première épaisseur est constituée d'une feuille métallique,
une deuxième épaisseur est constituée d'un matériau de liaison retardateur de flamme, et
une troisième épaisseur est constituée d'une pluralité de couches, chacune desdites couches comprenant un réseau de fibres polymères inflammables dans une matrice, lesdites fibres polymères ayant une ténacité d'au moins 17 g/denier, un module en traction d'au moins 500 g/denier et une énergie de rupture d'au moins 20 joules/g,
dans lequel la ténacité des fibres, le module en traction et l'énergie de rupture sont mesurés sur un fil par la méthode ASTM D2256 ;
dans lequel ledit matériau de liaison retardateur de flamme comprend des polymères intrinsèquement retardateurs de flamme sélectionnés parmi le polyéthylène chloré, le chlorure de polyvinyle, le poly(1,1-dichloroéthylène), le poly(chlorotrifluoroéthylène), le poly(1,1-dichloro-2-fluoroéthylène), le poly(1,2-dichloro-1,2-difluoroéthylène), le poly(1,1-difluoroéthylène), le poly(1,2-difluoroéthylène), le poly(tétrafluoroéthylène), le poly(trifluoroéthylène), le poly((pentafluoroéthyl)éthylène), le poly(tétradécafluoropentyléthylène), le poly(hexafluoropropylène), le poly(2,3,3,3-tétrafluoropropylène), le poly(3,3,3-trifluoropropylène), le poly(heptafluoropropyl)éthylène), le poly(fluorure de vinylidène) et le poly(tribromostyrol), des mélanges de ceux-ci, et des copolymères des monomères précédents comprenant ces polymères, et le mélamine-formaldéhyde, l'urée-formaldéhyde, le phénol-formaldéhyde,
autrement, ledit matériau de liaison retardateur de flamme comprend au moins 10 % en poids d'un matériau polymère sélectionné parmi des thermoplastiques et des matériaux thermodurcissables et un additif retardateur de flamme,

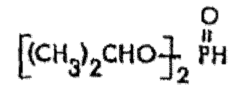
ledit additif retardateur de flamme étant sélectionné parmi les additifs organiques suivants :

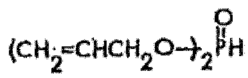
les composés suivants à **fonctionnalité P-H**

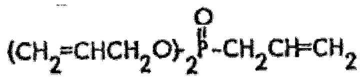


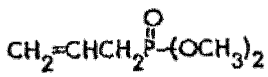


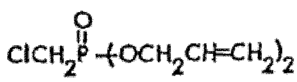


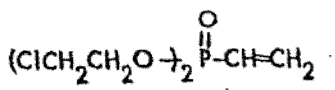


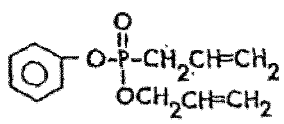




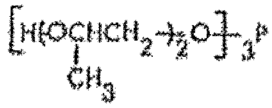








les composés suivants à **fonctionnalité -OH**



$$[H(OCH(CH_3)CH_2)_2O]_2P(=O)(CH(CH_3)CH_2O)_2H$$

$$(C_4H_9O)_2P(=O)H$$

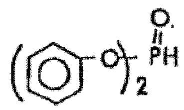
$$[CH_3(CH_2)_3O]_2P(=O)H$$

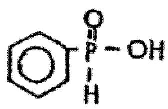
$$[CH_3(CH_2)_3CH(C_2H_5)-CH_2-O]_2P(=O)H$$

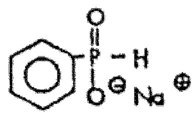
$$(C_8H_{17}O)_2P(=O)H$$

$$(C_{10}H_{21}O)_2P(=O)H$$

$$(C_{14}H_{29}O)_2P(=O)H$$





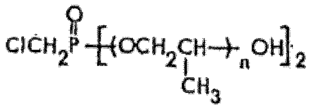


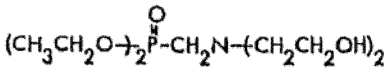
les composés suivants à **fonctionnalité CH_2=CH-**

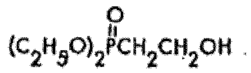
$$(CH_2=CHCH_2O)_3P$$

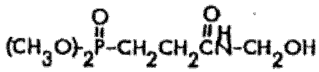
$$(CH_2=CHCH_2O)_3P=O$$

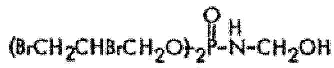
$$HOCH_2P(=O)[O(CH_2CH_2O)_3H]_2$$

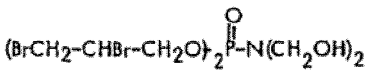


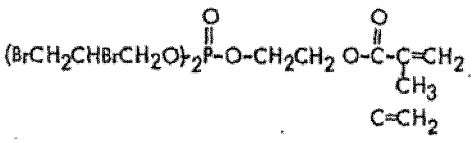




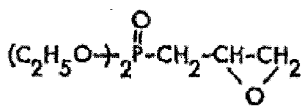


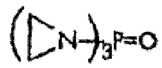


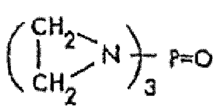




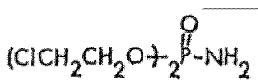
les composés suivants à **fonctionnalités**

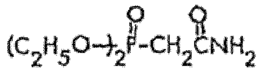


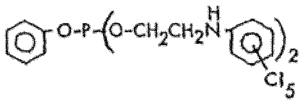


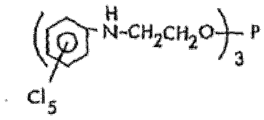


les composés suivants à **fonctionnalité -NH**

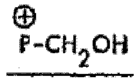


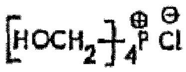






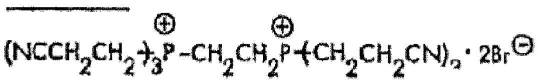
les composés suivants à **fonctionnalité**

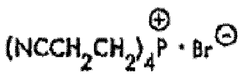


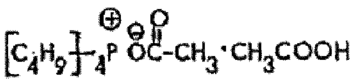


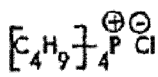
$\oplus P(CH_2OH)_4A\ominus$

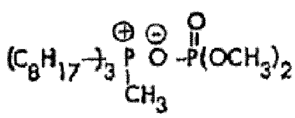
les composés sels de **$R_4P\oplus$** suivants



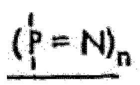


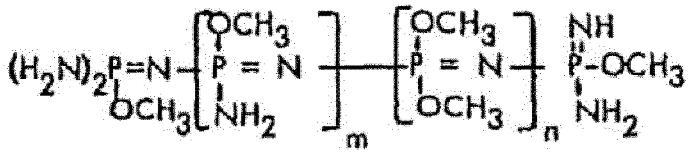


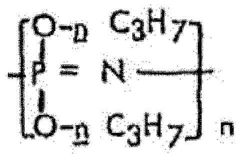




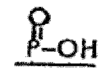
les composés polymères suivants contenant

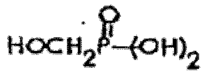


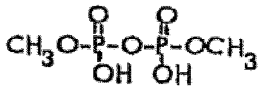


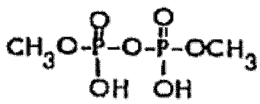


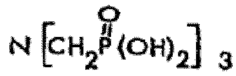
les composés suivants à **fonctionnalité**

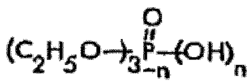




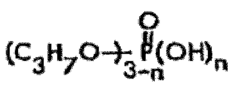








n = 1 à 2



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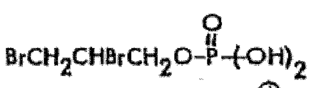
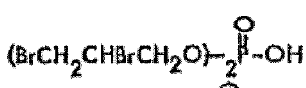
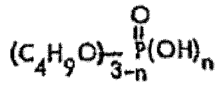


(et SEL de $NH_4^{\oplus}$)



(et SEL de $NH_4^{\oplus}$)



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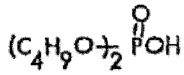

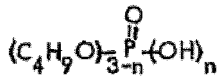

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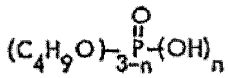

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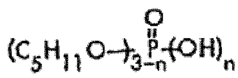

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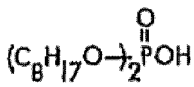
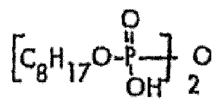
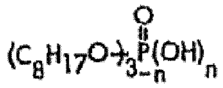
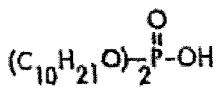
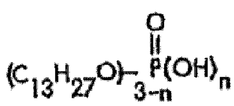






n = 1 à 2





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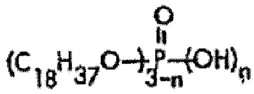
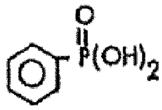
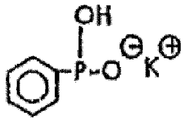
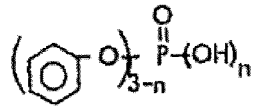


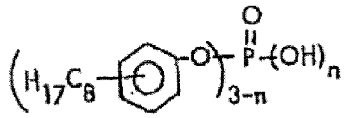
n = 1 à 2





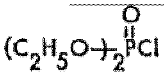


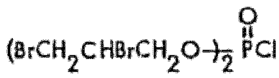
n = 1 à 2

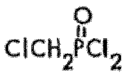


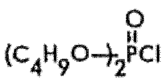
n = 1 à 2

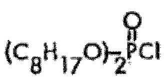
les composés suivants à **fonctionnalité P-Cl**

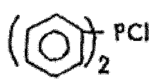








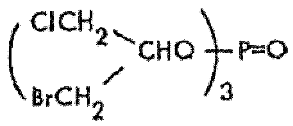




les composés suivants à **fonctionnalité P + S**

$(CH_3)_2P-S-S-P(CH_3)_2$

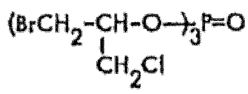
les composés suivants contenant **P + Br**

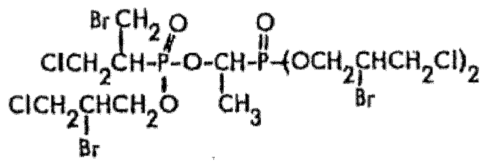


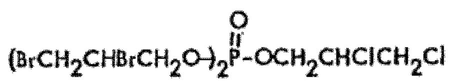
$(BrCH_2CHBrCH_2O)_3P=O$

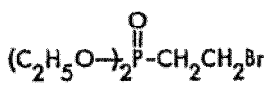
$(XCH_2CHXCH_2O)_3P=O$

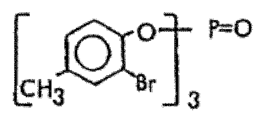
X = Cl, Br

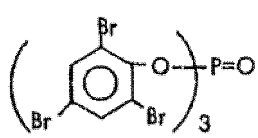












les composés suivants contenant **P + Cl**

$$(ClCH_2CH_2O)_3P$$

$$[(ClCH_2)_2CHO]_3P{=}O$$

$$(ClCH_2CHClCH_2O)_3P{=}O$$

$$(ClCH_2CH_2CH_2O)_3P{=}O$$

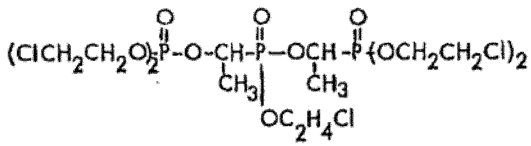
$$(ClCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}O)_3P{=}O$$

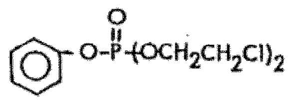
$$(CH_3CHClCH_2O)_3P{=}O$$

$$C_8H_{17}O{-}\overset{\displaystyle O}{\overset{\|}{P}}(OCH_2CH_2Cl)_2$$

$$ClCH_2CH_2\overset{\displaystyle O}{\overset{\|}{P}}(OCH_2CH_2Cl)_2$$

$$(ClCH_2)_2C\left[CH_2O\overset{\displaystyle O}{\overset{\|}{P}}(OCH_2CH_2Cl)_2\right]_2$$





les composés suivants contenant **P (Phosphites)**

$$(CH_3O)_3P$$

$$(CH_3CH_2O)_3P$$

$[(CH_3)_2CHO]_3P$

$[CH_3(CH_2)_3O]_3P$

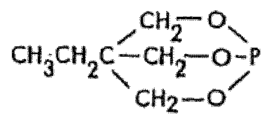
$(C_8H_{17}O)_3P$

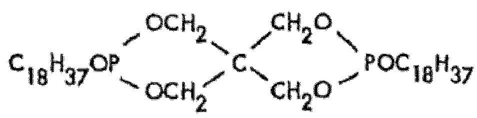
$[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_3P$

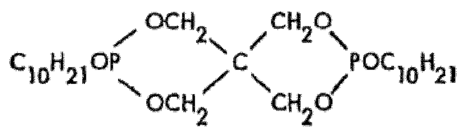
$(C_{12}H_{25}O)_3P$

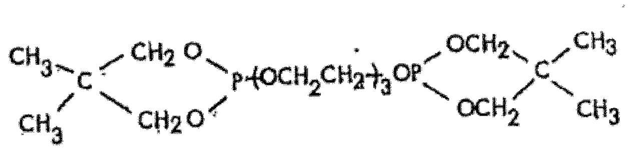
$(C_{18}H_{37}O)_3P$

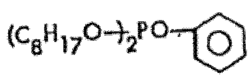
$(C_{18}H_{37}O)_3P$

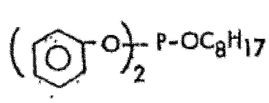


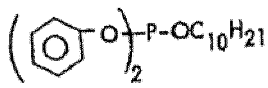


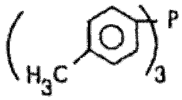












les composés suivants contenant **P (Phosphates)**

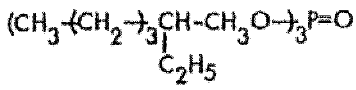
$(CH_3O-)_3P=O$

$(C_2H_5O)_3P=O$

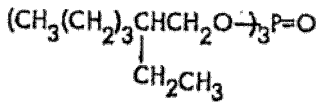
$(C_2H_5O-)_3P=O$

$(C_4H_9O-)_3P=O$

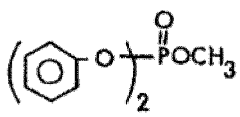
$(C_8H_{17}O-)_3P=O$

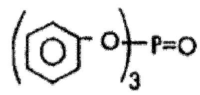


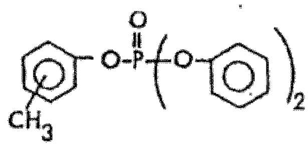
$(C_8H_{17}O-)_3P=O$

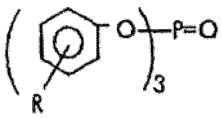


$(C_4H_9O-CH_2CH_2O-)_3P=O$



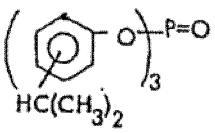


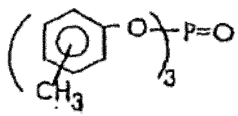


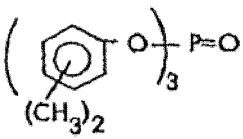


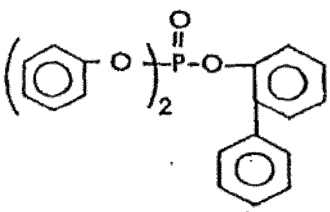
R = H, CH_3

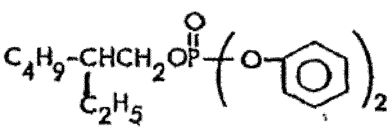
R=H, $(CH_3)_2CH$

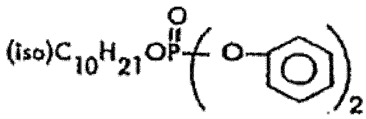












les composés suivants contenant **P (Phosphonates)**

$$(CH_3O\text{—})_2P(=O)\text{—}CH_3$$

$$(CH_3CH_2O\text{—})_2P(=O)\text{—}CH_2CH_3$$

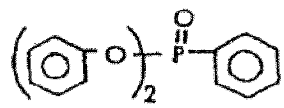
$$(C_2H_5O\text{—})_2P(=O)\text{—}CH_2COOC_2H_5$$

$$(CH_3O\text{—})_2P(=O)\text{—}CH_2CO_2CH_3$$

$$(C_2H_5O\text{—})_2P(=O)\text{—}CH_2CN$$

$$[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_2P(=O)\text{—}CH_2CH(C_2H_5)(CH_2)_3CH_3$$

$$[CH_3(CH_2)_3O]_2P(=O)\text{—}(CH_2)_3CH_3$$

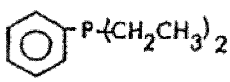


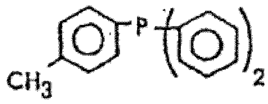
les composés suivants contenant **P (Divers)**

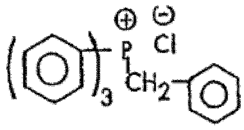
$$(C_2H_5O\text{—})_{1.5}P(=O)(ONH_4)_{1.5}$$

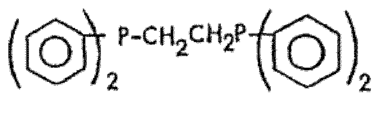
$$(n\text{-}C_4H_9)_3P{=}O$$

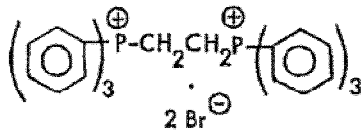
$$(n\text{-}C_8H_{17})_3P{=}O$$

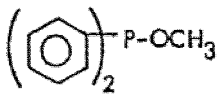


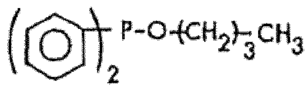


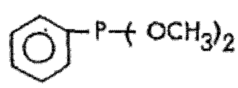


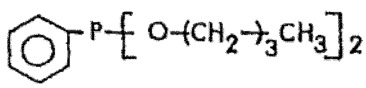












les composés suivants contenant **P + S**

$$(C_{12}H_{25}S)_3P$$

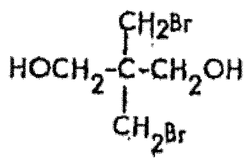
$$(CH_3CH_2O)_3P{=}S$$

$$[CH_3(CH_2)_3O]_3P{=}S$$

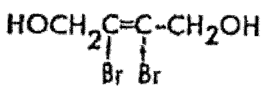
$$(C_8H_{17}O)_3P{=}S$$

les composés **bromés** suivants à **fonctionnalité -OH**

$$(BrCH_2)_3C{-}OH$$

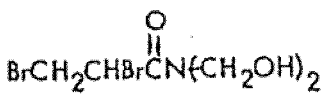


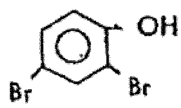
$$BrCH{=}CBr{-}CH_2OH$$

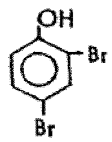


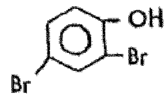
$BrCH_2CH_2OH$

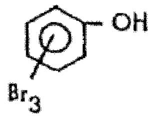
$BrCH_2CHBrCH_2OH$

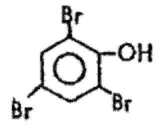


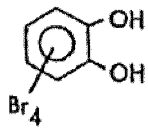


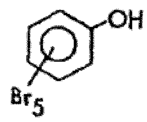


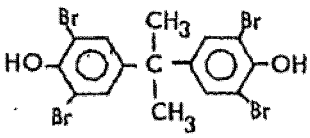


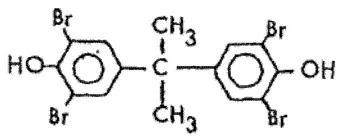


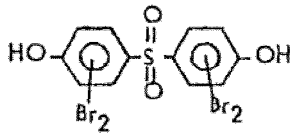


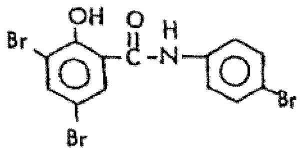


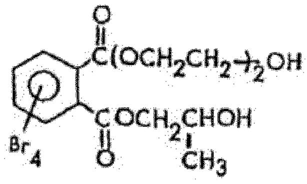


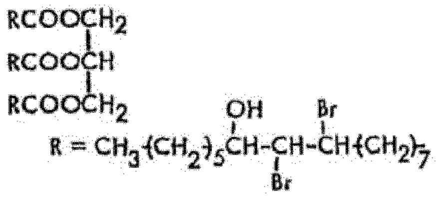


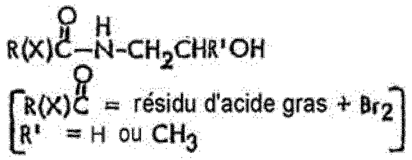


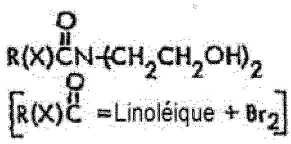


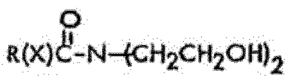


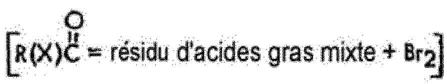




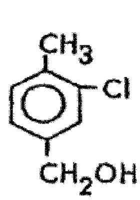


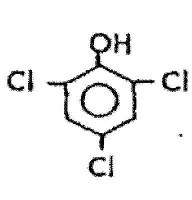


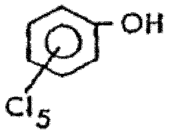


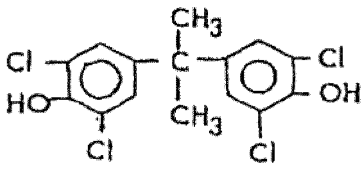


les composés **chlorés** suivants à **fonctionnalité -OH**

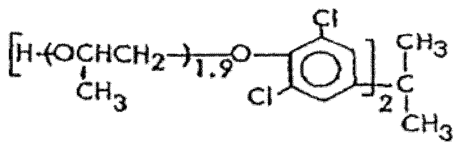


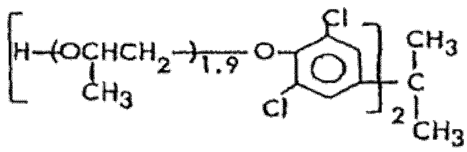


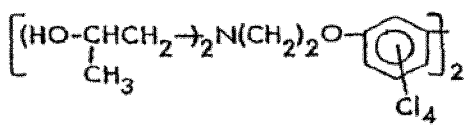


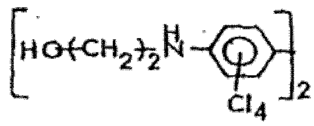


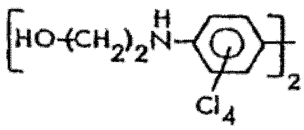
Produit de Cl_2 et

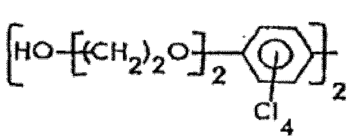








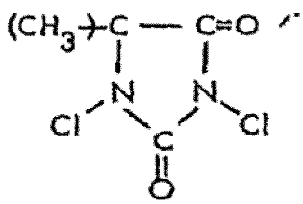


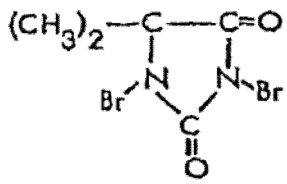


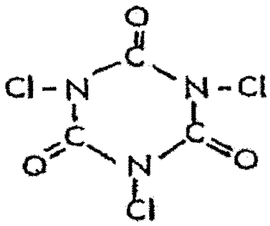
les composés suivants à **fonctionnalité -C≡C-**

$Cl\text{-}CH_2\text{-}C{\equiv}C\text{-}CH_2Cl$

les composés suivants à **fonctionnalité N-halogène-**

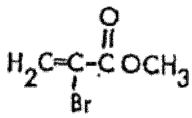


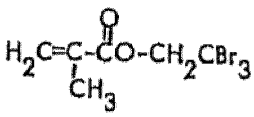


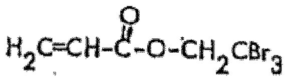


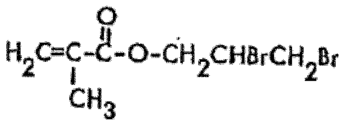
les composés suivants à **fonctionnalité** $H_2C{=}C$-

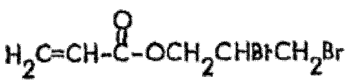
$CH_2{=}CH$-Br

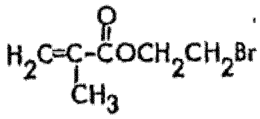


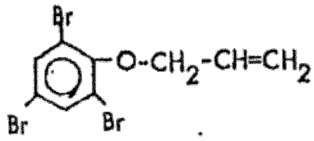


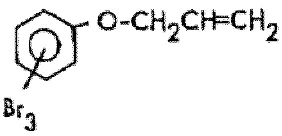


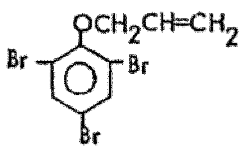


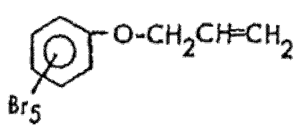


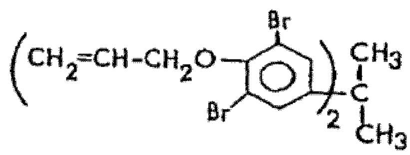


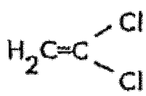






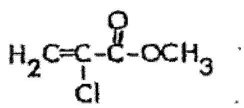


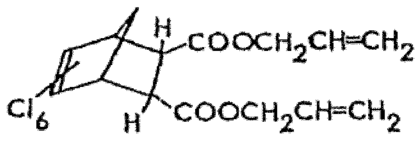


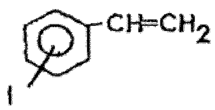


$CH_2=CCl_2$

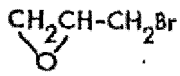
$CH_2=CH\text{-}CH_2Cl$

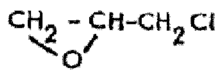


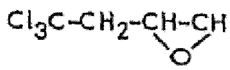


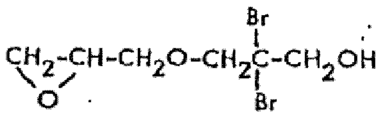


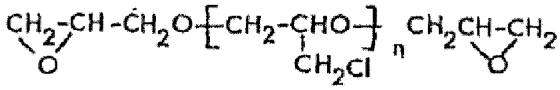
les composés suivants à **fonctionnalité**



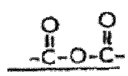


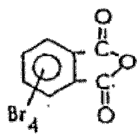


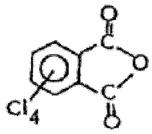


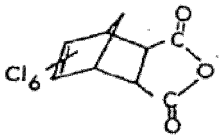


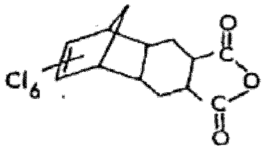
les composés suivants à **fonctionnalité**



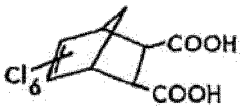


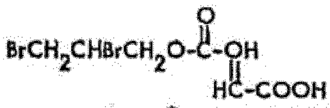






les composés suivants à **fonctionnalité -COOH**





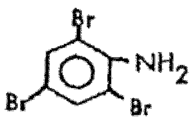
(et SEL de $NH_4^{\oplus}$)

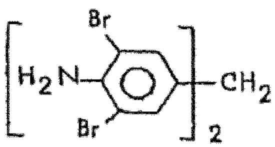
les composés suivants à **fonctionnalité -CHO**

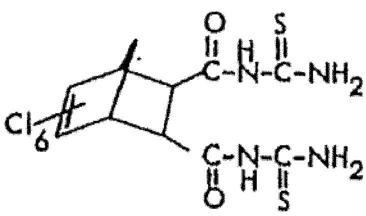
$BrCH_2CHBr\text{-}CHO$

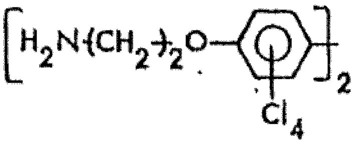
$Cl_3C\text{-}CHO$

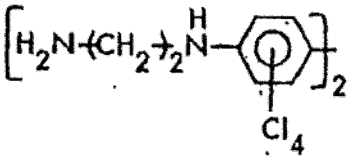
les composés suivants à **fonctionnalité -NH_2**

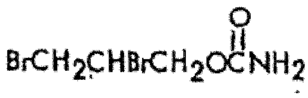












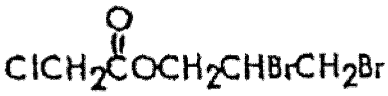
LES COMPOSÉS HALOGÉNÉS NON FONCTIONNELS SUIVANTS Composés bromés

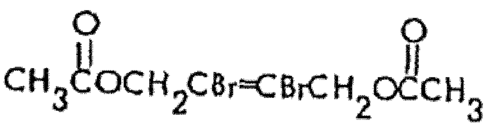
$BrCH_2Cl$

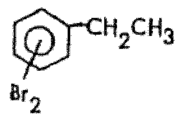
$Br_2CH\text{-}CHBr_2$

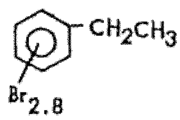
$BrCH_2CH_2CHCl$

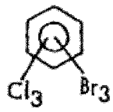
$BrCH_2CHBrCHBrCH_2Br$

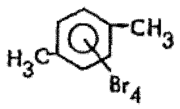


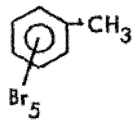


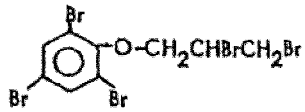


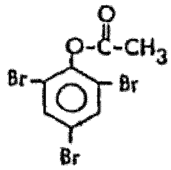


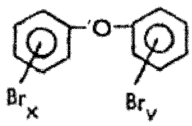




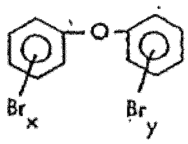




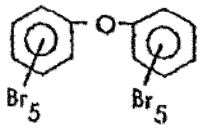


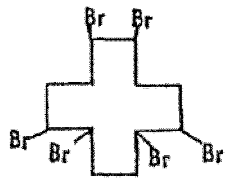


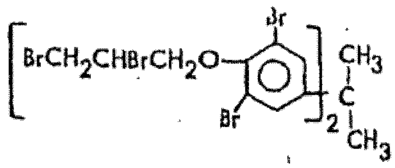
x + y = 5

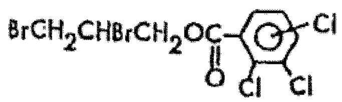


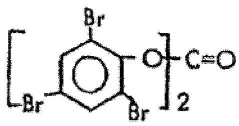
x + y = 8

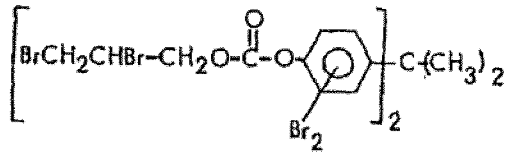


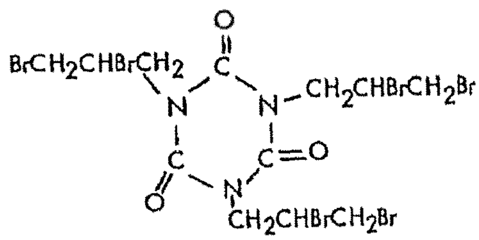


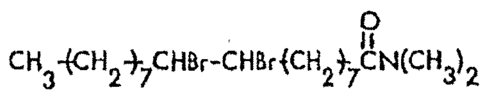










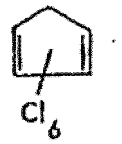


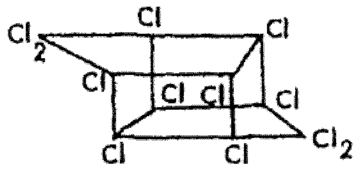
Composés chlorés

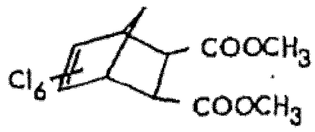
$Cl_3C\text{-}CCl_3$

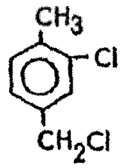
$ClCH_2CHClCH_2Cl$

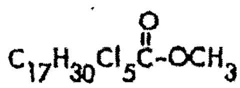
$Cl_2C{=}CCl\text{-}CCl{=}CCl_2$



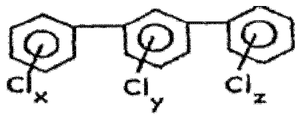




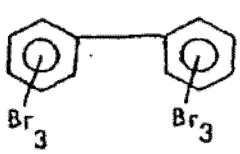


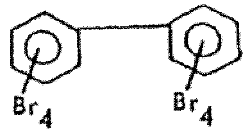


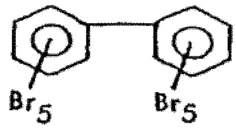
Chloro-triphényles (et à fonctionnalités supérieures)



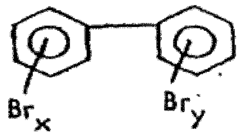
Bromo- et chloro- biphényles



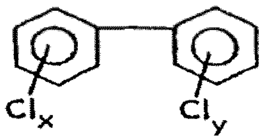




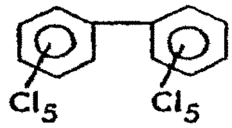
$X_6 = Cl$
$X_4 = Br$



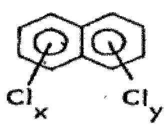
x + y = 8



(x + y = 1 - 10)



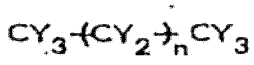
Chloro-naphtalènes



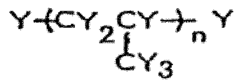
PARAFFINES HALOGÉNÉES

$$CY_3 \left(CY_2 \right)_n CY_3$$

Y = Br, H



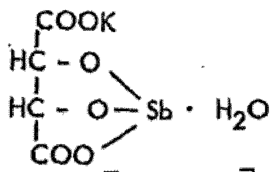
Y = H, Cl

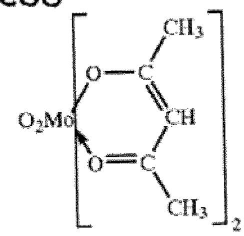


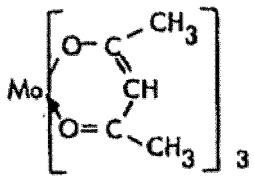
Y = H, Cl

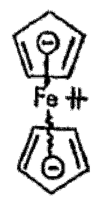
ou les additifs inorganiques suivants : oxyde d'antimoine, sulfures d'antimoine, halogénures d'antimoine, antimonite de sodium ou de potassium, phosphates d'ammonium, de sodium ou de potassium, halogénures de phosphore, chlorure phosphonitrilique, pentasulfure de phosphore, borates de sodium, tétrafluoroborate de sodium, de potassium ou d'ammonium, borates de calcium ou de baryum, tétraborate de lithium, de sodium ou de potassium, acide borique, triméthoxyborozine, hydrates d'oxyde d'aluminium, hydrates d'aluminophosphates, silicates de sodium, bromure d'ammonium, sulfate d'ammonium, silicates de lithium, oxyde de molybdène, paramolybdate d'ammonium, sulfure de molybdène, et sulfamide ;

ou les additifs organométalliques suivants :









et

dans lequel ledit réseau de fibres polymères inflammables comprend des fibres inflammables sélectionnées parmi des polyoléfines non modifiées, des polyesters, l'alcool polyvinylique et le polyacrylamide.

2. Article composite selon la revendication 1, constitué en outre d'une quatrième épaisseur comprenant un matériau de liaison retardateur de flamme tel que défini dans la revendication 1, et d'une cinquième épaisseur comprenant une feuille métallique.

3. Article composite selon la revendication 1, comprenant en outre une composition résineuse intumescente entre ladite première épaisseur et ladite deuxième épaisseur, dans lequel ladite composition résineuse intumescente comprend un agent gonflant sélectionné dans le groupe constitué de la mélamine, de sels de mélamine, de dérivés de mélamine, de l'urée, du dicyandiamide et de la guanidine, dispersé dans une résine sélectionnée dans le groupe constitué de polymères phénoliques, de polymères de mélamine, d'époxydes, de silicones, de polyesters insaturés et de polyuréthanes thermodurcissables.

4. Article composite selon la revendication 3, comprenant en outre une cinquième épaisseur constituée d'une composition résineuse intumescente, une sixième épaisseur constituée d'un matériau de liaison retardateur de flamme tel que défini dans la revendication 1, et une septième épaisseur constituée d'une feuille métallique,
dans lequel ladite composition résineuse intumescente comprend un agent gonflant sélectionné dans le groupe constitué de la mélamine, de sels de mélamine, de dérivés de mélamine, de l'urée, du dicyandiamide et de la guanidine, dispersé dans une résine sélectionnée dans le groupe constitué de polymères phénoliques, de polymères de mélamine, d'époxydes, de silicones, de polyesters insaturés et de polyuréthanes thermodurcissables.

5. Article composite selon la revendication 1 ou la revendication 3, dans lequel ladite feuille métallique est de l'aluminium ayant une épaisseur de 0,0005 pouce (12,7 micromètres) à 0,005 pouce (127 micromètres).

6. Article composite selon la revendication 1 ou la revendication 3, dans lequel ledit matériau de liaison retardateur de flamme est un mélange d'oxyde d'antimoine (Sb_2O_3), de décabromodiphényléther et de cire de paraffine polychlorée dans un liant de résine polyacrylate.

7. Article composite selon la revendication 1 ou la revendication 3, dans lequel lesdites fibres polymères inflammables sont en polyéthylène.

8. Article composite selon la revendication 7, dans lequel lesdites fibres de polyéthylène sont orientées unidirectionnellement à l'intérieur d'une couche, et dans lequel les fibres situées dans des couches adjacentes sont orientées à 90 ° les unes par rapport aux autres.

9. Article composite selon les revendications 3 ou 4, dans lequel ladite composition résineuse intumescente comprend en outre un composé dont la décomposition produit une masse de carbone qui est un composé organique polyhydroxylé.

10. Article composite selon la revendication 10, dans lequel ledit composé organique polyhydroxylé est sélectionné parmi le pentaérythritol, le dipentaérythritol, le tripentaérythritol, l'amidon ou un sucre.

11. Article composite selon l'une quelconque des revendications 3, 4, 9 et 10, dans lequel ladite composition résineuse intumescente comprend en outre une substance formant un acide qui est sélectionnée parmi un aminophosphate, des phosphates d'ammonium, des phosphates d'amines, des polyphosphates d'ammonium, et le phosphate de mélamine.

12. Article composite selon l'une quelconque des revendications 1 à 5 ou 7 à 11, dans lequel ledit matériau retardateur de flamme comprend un polymère intrinsèquement retardateur de flamme tel que défini dans la revendication 1.

REFERENCES CITED IN THE DESCRIPTION

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